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# Electrochemical Reactivity in Room-Temperature Ionic Liquids

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## 1. Introduction

Nonaqueous ionic liquids have been known for almost one century. In 1914, Paul Walden described the synthesis and properties of the “first” ionic liquid, ethylammonium nitrate. This salt displays a low melting temperature (12 °C) and was primarily prepared for electric conductivity measurements.<sup>1</sup> Paul Walden gave a definition of ionic liquids that is still acknowledged today.<sup>2</sup> They are “materials composed of cations and anions, that melt around 100 °C or below as a arbitrary temperature limit.” This definition identifies the difference from molten salts that have also been known for a long time and are inorganic salts with high melting temperatures.<sup>3</sup> Despite this early discovery, little attention has been paid to the ionic liquids, whereas the chemistry of inorganic molten salts and eutectics was significantly developed. These inorganic ionic liquids required high working temperatures (150–1000 °C), and their often corrosive nature has a deleterious effect on the reaction vessels. Then, research activity on room-temperature ionic liquids renewed with the discovery of alkylpyridinium or 1,3-dialkylimidazolium haloaluminate salts by groups in Colorado State University and in the Air Force Academy in the mid-1970s.<sup>4</sup> These salts were formed by mixing aluminum halides with the corresponding imidazolium or pyridinium halides. The first electrochemical studies about these new liquid [EtP][Br]–[AlCl<sub>3</sub>] salts were reported in 1975.<sup>5</sup> Interestingly, easy

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Corinne Lagrost was born in Evian (France) in 1972. She received a M.Sc. (1996) in Electrochemistry at Pierre et Marie Curie University (Paris) and then a Ph.D. from Denis Diderot University (Paris) in 2000 in the areas of conducting polymers and supramolecular chemistry (Electropolymerization of thiophenes— $\beta$ -cyclodextrin host—guest compounds). After postdoctoral work at the University of Amsterdam (The Netherlands), she took up a position at CNRS in 2001 (Chargée de Recherche). She currently works in the laboratory Sciences Chimiques de Rennes (Rennes) as senior scientist. Her research interests are the electrochemical reactivity in ionic liquids and the functionalization of conducting surfaces.

tuning of their Lewis acidity is possible from variations of the molar ratio of the two components. Unfortunately, these haloaluminate ionic liquids suffered from their high sensitivity to atmospheric moisture and required handling under strict anhydrous conditions to avoid their hydrolysis.

In the 1990s, a significant milestone was passed when the imidazolium salts incorporated the tetrafluoroborate or hexafluorophosphate anions.<sup>6,7</sup> Unlike their haloaluminate analogues, this new generation of room-temperature ionic liquids (RTILs) can be prepared, stored, and handled outside a glovebox. By a careful choice of the combination of these cations and anions, it was possible to prepare a large variety of ionic liquids that are liquid at and below room temperature. These pioneering works opened up avenues for a surge of research about the RTILs.<sup>8–16</sup>

Since 2000, more than 6000 papers have been dedicated to the field of ionic liquids, with more than 1000 in 2004, 1300 in 2005 and nearly 1900 in 2006.<sup>17</sup> In recent electrochemistry research papers, a larger and larger part is dedicated to the nonhaloaluminate RTILs, and it is likely that these air- and water-stable ionic liquids will dominate the field of RTILs in the future.<sup>18</sup>

There have been several reviews dealing with several aspects of nonhaloaluminate ionic liquids in physical chemistry<sup>19</sup> or more specifically concerning their interest in electrochemistry,<sup>14</sup> including their use as electrolyte materials,<sup>20,21</sup> their role in solution electrochemistry and some applications in electrosynthesis,<sup>18,22</sup> and their use in electrochemical devices.<sup>23</sup> In this review, we focus on electrochemical reactivity in the nonhaloaluminate ionic liquids with a particular emphasis about fundamental studies and suitability of electrochemical methods in relation to such investigations. In the first part of the review, we give an overview on the physicochemical properties of RTILs with a special interest about those that could influence the electrochemical reactivity in solution. Suitability of the electrochemical methods in RTILs and practical consequences of the special RTIL properties regarding the methodology are covered. Differences from conventional media and specific difficulties in the interpretation of the data are treated.

The second part of the paper is dedicated to electrochemical reactivity studies. An overview of the recent fundamental research related to the chemical reactivity, investigated with electrochemical methods, are presented. In most of these investigations, electrochemistry is a tool for studying the reactivity of intermediates. But the conclusions are obviously not limited to electrochemistry. In such a perspective, different general classes of reactions are examined to underline the main reactivity differences observed in RTILs and in conventional solvents. Starting from the basic diffusion phenomena, fundamental investigations about heterogeneous and homogeneous electron transfers are presented, to finish with some classical reactions triggered by an electron transfer. Finally, investigations related to applications of ionic liquids in bioelectrochemistry, in electrosynthesis, and in organic material preparations through electropolymerization are described.

## 2. Common Non-Haloaluminate Room-Temperature Ionic Liquids

Non-haloaluminate room-temperature ionic liquids (RTILs) considered in this review share a common general structure of a bulky unsymmetrical “onium” organic cation associated with a weakly coordinating organic or inorganic anion. So far, the most prevalent onium cations are the 1,3-dialkylimidazolium, *N,N*-dialkylpyrrolidinium, *N,N,N,N*-tetraalkylammonium, or *N*-alkylpyridinium cations. Concerning their anionic counterparts, tetrafluoroborate ( $\text{BF}_4^-$ ) hexafluorophosphate ( $\text{PF}_6^-$ ), bis(trifluoromethylsulfonyl)amide ( $\text{NTf}_2^-$ ), or triflate ( $\text{OTf}^-$ ) are the most popular anions. However, even restricted to electrochemical applications, it is far from possible to catalogue an exhaustive combination of cations and anions since numerous ionic liquid compounds have been studied in this regard. Table 1 gathers some cations and anions commonly used for the preparation of RTILs. A tendency to move toward less toxic fluorine-free anions, like amino acids,<sup>24</sup> or cations, like choline (vitamin B4), is now found in the field.<sup>25,26</sup>

**Table 1. Structures and Abbreviations for Commonly Occurring Cations and Anions**

Abbreviation	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
[HmIm]	H	CH <sub>3</sub>	H
[MmIm]	CH <sub>3</sub>	CH <sub>3</sub>	H
[EmIm]	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	H
[PmIm]	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	H
[BmIm]	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	H
[HexMIm]	CH <sub>3</sub>	C <sub>6</sub> H <sub>13</sub>	H
[BEIm]	C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	H
[EMMIm]	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>
[BMMIm]	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	CH <sub>3</sub>
[HexMMIm]	C <sub>6</sub> H <sub>11</sub>	CH <sub>3</sub>	CH <sub>3</sub>
[MPhMIm]	CH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	CH <sub>3</sub>
[EtP]	C <sub>2</sub> H <sub>5</sub>		
[BuP]	C <sub>4</sub> H <sub>9</sub>		
[PenP]	C <sub>5</sub> H <sub>11</sub>		
[HexP]	C <sub>6</sub> H <sub>13</sub>		
[Pyr <sub>2</sub> ]	C <sub>2</sub> H <sub>5</sub>		
[Pyr <sub>3</sub> ]	C <sub>3</sub> H <sub>7</sub>		
[Pyr <sub>4</sub> ]	C <sub>4</sub> H <sub>9</sub>		
[Pyr <sub>6</sub> ]	C <sub>6</sub> H <sub>13</sub>		
[Mc <sub>3</sub> BuN]	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	
[Et <sub>3</sub> BuN]	C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	
[MeBu <sub>3</sub> ]	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	
[Et <sub>3</sub> HexN]	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>13</sub>	
[Et <sub>3</sub> OctN]	C <sub>2</sub> H <sub>5</sub>	C <sub>8</sub> H <sub>17</sub>	
[NTf <sub>2</sub> ]			
[OTf]			
[PF <sub>6</sub> ]			
[BF <sub>4</sub> ]			
[AcO]			

RTILs have been attracting increasing interest in the past decade because of many unique properties that they are supposed to have. RTILs have negligible vapor pressure and are thus nonflammable and nonvolatile, largely decreasing the chance for fugitive emissions. They show a high thermal stability, with decomposition temperatures around 300–500 °C. They are able to solvate a large variety of organic and inorganic compounds, either polar or nonpolar. They are generally regarded as polar yet noncoordinating solvents. They display a good intrinsic conductivity and are extremely redox-robust. Actually, as a result of the intense research activity dealing with the study of their physicochemical

**Table 2. Viscosities for Some Representative RTILs at 20 °C**

RTIL	viscosity (mPa s) <sup>a</sup>
[BmIm][PF <sub>6</sub> ]	308
[BmIm][NTf <sub>2</sub> ]	52
[BmIm][OTf]	90
[BmIm][BF <sub>4</sub> ]	154
[EmIm][BF <sub>4</sub> ]	37–66.5
[EmIm][NTf <sub>2</sub> ]	32–34
[HexMIm][PF <sub>6</sub> ]	690
[HexMIm][NTf <sub>2</sub> ]	87
[HexMIm][BF <sub>4</sub> ]	314
[OctMIm][PF <sub>6</sub> ] <sup>b</sup>	866–857
[OctMIm][NTf <sub>2</sub> ] <sup>b</sup>	119
[OctMIm][BF <sub>4</sub> ] <sup>b</sup>	135
[DecMIm][NTf <sub>2</sub> ] <sup>c</sup>	152
[Et <sub>3</sub> Hex][NTf <sub>2</sub> ]	220
[HexP][NTf <sub>2</sub> ]	54
[OctP][NTf <sub>2</sub> ] <sup>b</sup>	134
[Pyr <sub>4</sub> ][NTf <sub>2</sub> ]	85
[Pyr <sub>3</sub> ][NTf <sub>2</sub> ]	63
[BMMIm][NTf <sub>2</sub> ]	105 <sup>d</sup>
[BMMIm][BF <sub>4</sub> ]	269 <sup>d</sup>

<sup>a</sup> Data taken from ref 30 and references therein. <sup>b</sup> Oct denotes the octyl group. <sup>c</sup> Dec denotes the decyl group. <sup>d</sup> Data taken from ref 45.

properties, it has become clear that these above-mentioned properties cannot be considered as generic properties for these media. For instance, it has been shown that many ionic liquids decompose above 80–90 °C and most decomposition temperatures reported in the literature are overestimates. Generally speaking, the properties that ionic liquids can possess strongly depend on the anion–cation combination, and ionic liquids can exhibit distinctly contrary properties. Thus, in a recent prospective paper, MacFarlane and Seddon point out that the only truly ubiquitous property of ionic liquids is that they exhibit ionic conductivity.<sup>27</sup>

### 3. Room-Temperature Ionic Liquids as Electrochemical Solvents

Work has been reported on the fundamental aspects of the physicochemical properties of ionic liquids.<sup>2,18–20,28,29</sup> It is important to consider these fundamentals in order to evaluate ionic liquids as possible powerful electrolytes. In this section, six topics, including viscosity, conductivity, diffusion of electroactive solutes, solvent properties, effect of impurities, and electrochemical window, were chosen to be developed, emphasizing their “electrochemical dimension”.

#### 3.1. Viscosity

As inferred from the two next sections, the viscosity is a property to consider for ionic liquids and probably corresponds to their major drawback, especially in electrochemistry. RTILs are viscous liquids, their viscosities being 1–3 orders of magnitude higher than those of conventional solvents.<sup>30</sup> This property is important in electrochemical studies because it may exert a strong effect on the rate of mass transport within solution and on the conductivity of the salts.

For a given cation, the viscosity of the RTILs is strongly determined by the nature of the anion.<sup>31–35</sup> The viscosity is lowest for RTILs containing the large [NTf<sub>2</sub>] anion and higher for RTILs containing nonplanar symmetric anions (Table 2). The most viscous ionic liquids are the [PF<sub>6</sub>]-containing ionic liquids. It has been suggested that the size, shape, and molar mass of the anion contribute to the viscosity



with smaller, lighter, and more symmetric anions leading to more viscous RTILs.<sup>36,37</sup> However, bis(perfluoroethylsulfonyl)imide anion, [BETI], leads to an increase of viscosity by  $\sim 100$  mPa s as compared with its smaller [NTf<sub>2</sub>] anionic parent,<sup>32,34</sup> indicating that other parameters need to be considered. Also, the relative basicity of the anions and their ability to form hydrogen bonds or to allow van der Waals attractions have a pronounced effect on viscosity.<sup>31,32</sup> The fluorinated anions such as [BF<sub>4</sub>], [PF<sub>6</sub>], or [BETI] form viscous ionic liquids due to the formation of hydrogen bonds or to increased van der Waals forces.<sup>31,32,34</sup> The weakly basic [NTf<sub>2</sub>] anion exhibits an extensive charge delocalization within the S–N–S backbone,<sup>38</sup> which decreases interactions in these salts, accounting for their low viscosity.<sup>31,32,39</sup> However, it is worth outlining that charge delocalization is a significant factor but is certainly not the only critical factor because a charge delocalization is also observed with [BETI].<sup>40</sup>

Cations also influence the viscosities of the RTILs. For any of the cation types, increasing the length of alkyl substituents results in increasing the viscosities because of stronger van der Waals interactions between larger cations.<sup>31,36,41,42</sup> The increase in viscosity for a series of 3-alkyl-1-methyl-imidazolium [NTf<sub>2</sub>] salts was found to be linear with the increase of the number of  $-\text{CH}_2$  groups, whereas a more complex behavior was associated with the corresponding [PF<sub>6</sub>] series.<sup>36</sup> Thus, the correlation of the physicochemical properties of RTILs with their structures implements a subtle balance between electrostatic and inductive forces.<sup>41</sup>

Branching of the alkyl chains in 1-alkyl-3-imidazolium RTILs reduces the viscosity.<sup>43</sup> In contrast, the introduction of a methyl group at the 2-position of the cation to form 1-alkyl-2,3-dimethyl-imidazolium induces an increase of the viscosity (Table 2). This result appears counterintuitive since the additional methyl group eliminates the possibility of forming a strong hydrogen-bonded interaction between the cation and the anion. From this H-bond suppression, a weaker cation–anion interaction is expected, leading to a significant decrease of the viscosity. Indeed, calculations performed on [BMIm][Cl] and [BMMIm][Cl] salts have demonstrated that the strength of the cation–anion interaction became weaker in the [BMMIm][Cl] as compared with [BMIm][Cl], but [BMMIm][Cl] exhibits a higher viscosity than [BMIm][Cl].<sup>44</sup> Two different main factors were demonstrated to contribute to an increase of the viscosity.<sup>44</sup> First, a significant decrease of entropy in the methylated salt has been evidenced due to a restricted number of ion-pair conformers that could be formed.<sup>44</sup> Such reduced ion-pair configurational variations result in more order within the ionic liquid. Second, the butyl chain rotation is inhibited because of steric repulsion from the methyl group,<sup>44</sup> and this has also been demonstrated to participate to an increase of the molecular arrangement. When the molecular order is high within the ionic liquid, the viscosity is increased.<sup>44</sup>

A significant decrease of viscosity is generally observed in ionic liquids as the temperature increases.<sup>30,45</sup> An Arrhenius-type relationship (Guzman–Andrade law,  $\eta = A e^{E_a/RT}$ , where  $E_a$  is the activation energy for viscous flow) was followed by most ionic liquids, while some others were better fitted with the Vogel–Tamman–Fulcher (VTF) equation ( $\eta = \eta_0 e^{B/(T-T_0)}$ , where  $\eta_0$  (mPa s),  $B$  (K), and  $T_0$  (K) are constants). Those RTILs that obeyed the Arrhenius law typically contained asymmetric cations without functional groups in the alkyl chains. The VTF model accurately

described the RTILs containing small, symmetrical cations with low molar mass.<sup>45</sup> However, it is worth indicating that the two behaviors are linked since the Arrhenius-type relationship is simply the higher temperature limit of the VTF equation.

As a general conclusion, it can be said that electrostatic interactions dominate the characteristic physicochemical properties of RTILs and distinguish them from common organic solvents. But, by consideration of RTILs of similar structures, the differences in the viscosity are mainly influenced by hydrogen bonding and van der Waals interactions.<sup>31,41</sup>

## 3.2. Conductivity

For any electrochemical process, the conductivity is a property of primary importance and the conductivity of the RTILs has been reviewed on several occasions, for example refs 20, 46, and 47. Being composed entirely of ions, RTILs are supposed to be among the most concentrated electrolytic fluids with many charge carriers per unit volume. When these charge carriers are mobile, very high conductivities are possible. Room-temperature ionic liquids exhibit conductivities in the broad range  $0.1\text{--}20\text{ mS cm}^{-1}$ .<sup>20,31,48</sup> Rather high conductivities of the order of  $10\text{ mS cm}^{-1}$  can be found in the imidazolium family.<sup>49</sup> Quaternary ammonium ionic liquids are always characterized by lower conductivities;  $2\text{ mS cm}^{-1}$  is thus the highest conductivity found for a *N,N*-dialkyl-pyrrolidinium [NTf<sub>2</sub>] salt.<sup>48,50–52</sup> It is worth mentioning that ionic liquids incorporating the tricyanomethanide anion and the dicyanamide anion possess some of the highest conductivities (up to  $36\text{ mS cm}^{-1}$ ).<sup>53–55</sup> But these values are considerably lower than those of concentrated aqueous electrolytes (for example, the aqueous KOH solution (29.4 wt %) applied in alkaline battery is  $540\text{ mS cm}^{-1}$ ).

The high viscosity of the RTILs has a major impact on the conductivities because the conductivity is inversely linked to the viscosity.<sup>32,37,41,51</sup> The less viscous [NTf<sub>2</sub>] salts usually exhibit among the highest conductivities.<sup>48</sup> Although a correlation between viscosity and conductivity is generally observed, the viscosity alone cannot account for the conductivity behavior. For instance, [EMIm][OTf] and [BMIm][NTf<sub>2</sub>] display similar viscosities and densities, but their conductivities differ by a factor of 2 (Table 3).<sup>31</sup> Many others factors contribute to the conductivity. Besides the effects of the ion size,<sup>31,32,35,56</sup> of the anionic charge delocalization,<sup>31,56</sup> and of the RTILs' density,<sup>32,35,41</sup> aggregation and correlated ionic motions have to be stressed.<sup>34,37,39,57</sup>

Transport properties and conductivities in a family of dialkylimidazolium RTILs were examined by varying the alkyl chain or the anion.<sup>37,56</sup> Increasing the length of the alkyl chains results in a higher viscosity and a lower conductivity. Increasing the size of the anions lowered the viscosity, but the conductivities, directly measured, were similar for any of the anions. However, conductivities calculated from the diffusion coefficients of the anions and the cations gave higher conductivities for the less viscous salts (larger anion).<sup>57</sup> The inconsistency between calculated conductivities from diffusion measurements and measured conductivities was attributed to correlated ion motion or the diffusion of neutral species or both. Strong ionic association (ion pairing) was found for the more viscous salts. While the diffusion coefficients of such neutral species or ion pairs can be measured, they do not contribute to conductivity due to their lack of net ionic charge. In addition to the formation

**Table 3. Physico-chemical Properties Data<sup>a</sup> for Two Families of Imidazolium Salts**

	<i>T</i> (°C)	viscosity (mPa s)	conductivity (S m <sup>-1</sup> )	density (g cm <sup>-3</sup> )	molecular weight (g mol <sup>-1</sup> )	molar concentration (mol L <sup>-1</sup> )
[EMIm]						
[BF <sub>4</sub> ]	25	37–66.5	1.58–1.38	1.28	197.97	6.46
[NTf <sub>2</sub> ]	25	28–34	0.91	1.52	391.32	3.88
[PF <sub>6</sub> ]	26		0.52	1.52	256.13	6.01
[OTf]	22	45	0.86	1.39	260.24	5.34
[BMIm]						
[BF <sub>4</sub> ]	25	154	0.35	1.26	226.01	5.575
[NTf <sub>2</sub> ]	25	52	0.40	1.43	419.37	3.41
[PF <sub>6</sub> ]	25	308	0.146–0.1	1.35	284.18	4.75
[OTf]	25	90	0.29	1.29	288.29	4.48

<sup>a</sup> Data taken from refs 30 and 58 and references therein.

of ion pairs, this work highlighted the basic idea of correlated ionic motion. Because of the proximity of the ions to one another in the ionic liquids, the random motion of one ion creates a high probability of a counterion motion in the same direction, which results in a mechanism of correlated pair motion, without requiring any existence of bonded species even on a transient basis.<sup>37</sup>

An equivalent rationale was recently used to understand the higher conductivities of [EMIm][BF<sub>4</sub>] and [BuP][BF<sub>4</sub>] compared with their corresponding [EMIm][NTf<sub>2</sub>] and [BuP][NTf<sub>2</sub>] salts.<sup>39</sup> Pulsed-gradient spin–echo NMR measurements and impedance spectroscopy studies showed that stronger cation–anion association occurs in [EMIm][NTf<sub>2</sub>] and [BuP][NTf<sub>2</sub>] than in [EMIm][BF<sub>4</sub>] and [BuP][BF<sub>4</sub>].<sup>39</sup> The degree of “ionicity” was evaluated to be around 0.6–0.8 for the latter and fell to 0.3–0.5 for the former. Since ionic aggregates that form neutral species or ion pairs cannot contribute to the ionic conductivity, the [NTf<sub>2</sub>] salts exhibit lower conductivities than the corresponding [BF<sub>4</sub>] salt. It is worth outlining that this work takes the opposite view to most published studies in the field. Instead of considering weak cation–anion interaction with NTf<sub>2</sub><sup>−</sup>, a strong ionic interaction with this anion is put forward.<sup>39</sup> The authors proposed that this strong ion-pair association is responsible for the lower viscosity of the [NTf<sub>2</sub>] salts because the presence of ion-pair associations and neutral ion aggregates would dilute the ionic concentration. Thus, the Coulombic interactions within the ionic liquid would be reduced,<sup>39</sup> which in turn would induce a decrease of the viscosity. On one hand, despite these explanations disagreeing with the most prevalent hypotheses (see above), further examinations of data gathered in Table 3 show that [BF<sub>4</sub>] salts always possess high “anomalous” conductivities compared with their parent [NTf<sub>2</sub>] and [PF<sub>6</sub>] salts, at variance of viscosity and molar concentration. On the other hand, the conclusions of Noda et al.<sup>39</sup> imply that [EMIm][PF<sub>6</sub>] should exhibit a higher conductivity than [EMIm][NTf<sub>2</sub>], which is not the case as shown in Table 3. No viscosity data are available for this [PF<sub>6</sub>] salt, but it is reasonable to consider that this salt would be more viscous than the [NTf<sub>2</sub>] one.

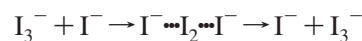
The dilution of neat ionic liquids in molecular liquids or, in some cases, the addition of small cations (Li<sup>+</sup>) brings about an increase in conductivity suitable for applications in batteries or double-layers capacitors.<sup>35,59–61</sup> However, at room temperature, the conductivity of neat ionic liquids is high enough for electrochemical experiments to be achieved in these media as in conventional organic electrolytes (molecular organic solvent with supporting salts). Ionic liquids take advantage of this intrinsic property. They can play the role of both solvent and supporting salts without

the need for adding any extraneous salts for performing electrochemical experiments.

### 3.3. Diffusion of Electroactive Solutes

Study of the transport of solutes concerns with fundamental aspects of electrochemical measurements in RTILs. Various electrochemical techniques are available to determine the diffusion coefficients of electroactive species in RTILs including microelectrode chronoamperometry, cyclic voltammetry, square wave voltammetry, impedance spectroscopy, and polarization measurements at thin layer cells.<sup>62–66</sup> A recent work evaluated the reliability and performance of four different methods by measuring the diffusion coefficients of triiodide in a mixture of two imidazolium-based ionic liquids.<sup>62</sup> The reproducibility of all methods is comparable, and the determined diffusion coefficients are on the order of  $1 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>.<sup>62</sup> This is a typical diffusion coefficient in RTILs. As examples, similar values have been measured for larger organic molecules such as ferrocene,<sup>63,64,67,68</sup> tetrathiafulvalene,<sup>63</sup> *N,N,N',N'*-tetraalkyl-phenylenediamine,<sup>69</sup> and some aromatic compounds.<sup>67</sup>

It is worth outlining that these diffusion coefficients value, commonly found in the RTILs, are about 2 orders of magnitude lower than those measured in conventional organic electrolytes. Of course, the slow diffusion observed in the RTILs is strongly related to the high viscosity of these media. The diffusion coefficients of *N,N,N',N'*-tetramethyl-*para*-phenylenediamine (TMPD) and *N,N,N',N'*-tetrabutyl-*para*-phenylenediamine (TBPd) were determined using microelectrode chronoamperometry for a series of RTILs of increasing viscosity, [EMIm][NTf<sub>2</sub>], [BMIm][NTf<sub>2</sub>], [OctMIm][NTf<sub>2</sub>], [DecMIm][NTf<sub>2</sub>], and [Et<sub>3</sub>HexN][NTf<sub>2</sub>].<sup>69</sup> For both compounds, the diffusion coefficients were found to be inversely proportional to the viscosity in agreement with the Stokes–Einstein equation:  $D = k_B T / (p \pi \eta r)$  where  $k_B$  is the Boltzmann constant,  $T$  the absolute temperature,  $\eta$  the viscosity,  $r$  the hydrodynamic radius, and  $p$  a constant equal to 4 or 6, depending on whether slip or stick conditions applied.<sup>41,69</sup> This conformity to the Stokes–Einstein relation qualitatively demonstrates that RTILs behave just as conventional solvents. However, Zistler et al. evidence a non-Stokesian transport behavior of the triiodide anion in [PMIm][I]/[BMIm][BF<sub>4</sub>] blends.<sup>62</sup> The I<sub>3</sub><sup>−</sup> transport is better described as a Grotthuss-type self-exchange mechanism:



An unexpected concentration dependence on the diffusion of ferrocene was reported in three different imidazolium RTILs, namely, [BMIm][NTf<sub>2</sub>], [BMIm][PF<sub>6</sub>], and [BMIm]-

[BF<sub>4</sub>].<sup>70–72</sup> Brooks and Doherty reported a small but linear increase with low ferrocene concentrations (<35 mM), which progressed to an exponential increase at higher concentrations, claiming a “super-concentration dependency”.<sup>72</sup> A similar behavior was also shown in [BMIm][PF<sub>6</sub>] except that a plateau was observed in higher concentrations.<sup>70</sup> A more linear variation over the 4–32 mM concentration range was found in a carefully purified [BMIm][BF<sub>4</sub>] salt, even if the diffusion coefficient seems to increase considerably for concentrations above 15 mM.<sup>71</sup> For any of these studies, no definite explanation for this effect could be provided. In contrast to these works, Compton et al. did not observe such an enhancement of the diffusion rate for the TMPD system in [Pyr<sub>4</sub>][NTf<sub>2</sub>] over a concentration range of 5–40 mM.<sup>73</sup>

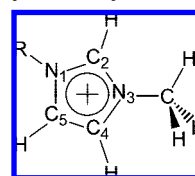
A spectacular dissimilarity in the diffusion coefficients between reactant and electrogenerated species was revealed for the one-electron reduction of dioxygen to superoxide in [EMIm][NTf<sub>2</sub>] and [Et<sub>3</sub>HexN][NTf<sub>2</sub>], as well as in [BMIm][NTf<sub>2</sub>] and [Et<sub>3</sub>BuN][NTf<sub>2</sub>].<sup>74,75</sup> While the superoxide appears to be stable in these media, its diffusion rate is lowered by more than 1 order of magnitude compared with that of dioxygen.<sup>74,75</sup> As a result, cyclic voltammetry produced from this couple displays both steady-state and transient behaviors. The reduction of oxygen to superoxide is dictated by radial diffusion to the electrode surface, and the forward scan is transient-shaped. In contrast, the reoxidation wave is controlled by linear diffusion and therefore is strongly peak-shaped.<sup>74</sup> Regarding the size of the reactant and its electrogenerated species, the dioxygen system can be considered a rather extreme case. Nevertheless, such dissimilarity has been also measured for the oxidation of TMPD to its radical cation and dication in four RTILs sharing the same [NTf<sub>2</sub>] anion. The ratio in diffusion coefficients of the radical cation and dication to the neutral molecules were determined to be 0.5 and 0.33.<sup>73</sup> Even stronger effects might be observed when the nature of the RTIL anion is varied or with strongly charge-localized compounds. The major concern of this dissimilarity is connected to the modeling of voltammetric data, for which assumption of equal diffusion coefficients is usually postulated by the electroanalyst. This assumption is then shown to be potentially unwise in the ionic liquids.

To extend the investigation into more fundamental analysis of the diffusion behavior in RTILs, Compton et al. studied the *translational* and the *rotational* diffusion coefficients of the radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) in five different RTILs of increasing viscosity.<sup>76</sup> A classical Stokes–Einstein behavior was observed and a fairly good agreement between *translational* and *rotational* diffusion activation energies was found except for a phosphonium-based RTILs. Because the phosphonium cation bore long alkyl chains, a bilayer-type structure was suggested to favor rotation with respect to translation, exemplifying a “microenvironment” effect in the RTILs.

### 3.4. Solvent Properties, Structural Aspects, and Specific Solvation Effects

This point is not restricted to electrochemistry.<sup>29</sup> Considering the structural aspects of the ionic liquids is usually helpful for the rationalization of physical and chemical processes occurring in the RTILs. In RTILs, there is a complex interplay of forces (Coulombic, van der Waals (dipole–dipole, dipole–induced dipole, dispersion), hydrogen bond, and possible  $\pi$ – $\pi$  or  $n$ – $\pi$  stacking), which controls the solvation

**Scheme 1. The 1-Alkyl-3-methylimidazolium Cation<sup>a</sup>**



<sup>a</sup> R = alkyl chain.

in these media.<sup>77</sup> Many fundamental studies using both theoretical and experimental (FTIR, Raman, NMR, fluorescence, etc.) methods have been undertaken to elucidate the structure–physicochemical properties relationship of ionic liquids. Only a limited number of examples will be quoted here, a comprehensive overview of the subject being beyond the scope of this review. Because they are intensively used, the imidazolium salts are the most widely studied. Consequently, many results reported in the following deal with this class of RTILs.

The first among all attributes of any solvent is its solvation ability. To quantify this property, solvent polarity is the most commonly used criterion. Despite this criterion being absolutely inappropriate for ionic liquids, because an ion does not have a well-defined dipole moment, many papers deal with this property in RTILs but also, more generally, with the solvent–solute interactions. The dynamic aspect of solute solvation has been considered as well. As examples, solvation thermodynamics,<sup>78</sup> solvent–solute interaction or polarity,<sup>77,79–87</sup> solvation dynamics, and conformational or surface structures<sup>88–98</sup> have been studied. All these studies concluded that the RTILs are, with no doubt, polar solvents, exhibiting a high polarizability. But recent works focusing on imidazolium, pyrrolidinium, pyridinium, quaternary ammonium, and sulfonium [NTf<sub>2</sub>] salts studied the static dielectric response of these RTILs and classified them as solvents of moderate polarity, corresponding to alcohols like *n*-hexanol.<sup>83,99</sup> It has been also demonstrated that RTILs can act as hydrogen-bond donors and acceptors. The basicity of RTILs depends on the nature of the anion while the hydrogen-bond acidity is more related to the nature of the cation, but it is balanced by the anion, or even by the presence of water.<sup>100</sup> Dynamic studies examined the time–length scale of solvent–solute interaction. They show that the solvation dynamics is multimodal (diffusion, collective motion, ion-pairing, friction, etc.) and occurs over a wide range of time scales, from femtoseconds to nanoseconds.<sup>88</sup>

A key to understanding the solvation ability of RTILs is provided by their liquid structure. Regarding the pure ionic character of the RTILs, the formation of ion pairs is expected to be an essential feature for describing solvation in RTILs as well as solvation of RTILs in other media. The formation of ion pairs in 1-alkyl-3-methylimidazolium salts containing various anions, Cl<sup>−</sup>, PF<sub>6</sub><sup>−</sup>, NTf<sub>2</sub><sup>−</sup>, or BF<sub>4</sub><sup>−</sup>, has been demonstrated by NMR,<sup>101–104</sup> FTIR,<sup>105,106</sup> neutron diffraction,<sup>107–109</sup> and calculations.<sup>106,110–115</sup> These investigations showed evidence for strong hydrogen-bonding-type interactions, C–H...F or C–H...Cl, involving the C<sub>2</sub>H (Scheme 1) proton of the imidazolium cation.

A deeper insight into the exact chemical nature of this interaction has been carried out from theoretical calculations, considering [EMIm][Cl] and [BMIm][Cl].<sup>111,112</sup> These studies demonstrated that the hydrogen bond is primarily ionic with a moderate covalent character. The Coulombic attraction



is the dominant stabilizing force, but the charge transfer and orbital interaction can contribute significantly. In the case of 1-butyl-3-methyl-imidazolium tetraphenylborate ionic liquid, a closely related C—H $\cdots\pi$  interaction was also reported between the hydrogens of the imidazolium cations and the phenyl ring of the tetraphenylborate anion.<sup>103</sup> Experimentally, these specific cation–anion interactions, easily evidenced in crystalline solid phase, were still found to occur in solution, especially in low dielectric media.<sup>101,103,105,106,116</sup>

Interestingly, neutron diffraction studies of some neat RTILs, supported by solid phase crystal structures analyses, indicated that charge ordering endured in the liquid phase.<sup>107–109</sup> Different 1,3-dimethyl-imidazolium salts, namely, [MMIm][Cl], [MMIm][PF<sub>6</sub>], and [MMIm][NTf<sub>2</sub>], have been studied. For the [Cl] and [PF<sub>6</sub>] salts, the molecular packing and interactions in the first two or three coordination shells were similar both in the crystal and in the liquid, although the atomic distances were altered in the liquid.<sup>107,109</sup> In comparison, the [NTf<sub>2</sub>] salt showed smaller charge ordering<sup>108</sup> because of the diffuse charge density and larger size of the [NTf<sub>2</sub>] anion.<sup>40</sup> Moreover, its liquid structure was poorly correlated to its crystal structure.<sup>117</sup> This was attributed to the conformational flexibility of the [NTf<sub>2</sub>] anion.<sup>108,117</sup> Nevertheless, it remains that ionic liquids form “quasimolecular” structures through three-dimensional networks of anions and cations. These hydrogen-bonded structures are maintained to a great extent even in solution in solvents of low dielectric media, making the RTILs highly organized media. Addition of solute within the RTILs causes a disruption of this original organization and modifies the liquid structure, depending of the respective affinities of both anion and cation toward the solute. For example, in [BMIm][BF<sub>4</sub>], water was shown to replace the C<sub>2</sub>—H $\cdots$ F interactions with hydrogen bonds involving water as an acceptor toward the [BMIm] cation and as a donor toward the [BF<sub>4</sub>] anion.<sup>102</sup> However, the disruption was suggested to not fully break down the Coulombic ordering of ions in the liquid, and a theoretical model was recently proposed to support this statement.<sup>118</sup> By considering a neutral dipolar solute, the author suggested that the solute was viewed as intercalating in the charge distribution of the neat liquid in a way that did not greatly perturb the electrostatic organization. In other words, the addition of a solute would not lead to polarization of the medium. Although very interesting, this model still has to be assessed and compared with more experimental data. Particularly instructive would be the consideration of charged solutes.

The structural organization of the RTILs is prone to spatial heterogeneity. Both molecular dynamics simulations<sup>119,120</sup> and experimental optical Kerr effect spectroscopy investigations<sup>121</sup> demonstrated the occurrence of heterogeneous domains in 1,3-dialkyl imidazolium salts. Provided that alkyl chains are longer than propyl, these domains are formed by side-chain aggregation of the alkyl groups with the cation ring and anions homogeneously distributed.<sup>121</sup> Henceforth, the RTILs, at least the imidazolium family, are better described as a “nanostructured” fluids.<sup>119,121</sup> It is claimed that these spatial heterogeneities offer a framework for interpreting the various dependences of the viscosity, conductivity, density, or polarity on the alkyl chain length and anion nature. Unlike the imidazolium family, less work has been done to study the cation–anion interaction within other kinds of ionic liquids. It is likely

that models developed for imidazolium salts, such as those we briefly mentioned above, can be extended to the other RTILs. However at this point, lack of data does not allow statement of a fully general picture of the RTIL liquid structure.

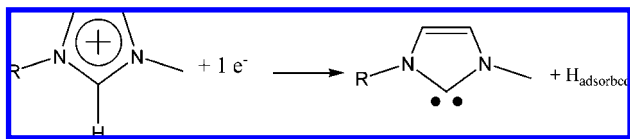
### 3.5. Effects of Impurities

The RTILs under consideration are described to be air- and moisture-stable. However, many of the imidazolium and ammonium salts are highly hygroscopic, and even hydrophobic RTILs are able to absorb water from the atmosphere.<sup>122,123</sup> While it is true that these ionic liquids do not undergo any of the hydrolysis problems that make the haloaluminates so difficult to handle, hydration may be a problem. This depends on the use to which the ionic liquid is being put and on the degree to which the solutes are sensitive to water. Electrochemically speaking, water impurities have been shown to decrease the viscosity,<sup>30,32,124</sup> to increase the conductivity,<sup>32,125</sup> and to shrink significantly the electrochemical window.<sup>32,65</sup> The addition of more than 3 wt % of water to [BMIm][BF<sub>4</sub>] and [BMIm][PF<sub>6</sub>] caused a decrease in the electrochemical window of over 2 V.<sup>65</sup> The traces of water also modified the rate of diffusion of species dissolved in the ionic liquids. The diffusion coefficient of *N,N,N',N'*-tetramethyl-*para*-phenylenediamine (TMPD) nearly doubles, while an even stronger increase was observed for the diffusion coefficients of methylviologen.<sup>65</sup> Although water is by far the major impurity affecting the RTILs, oxygen is also easily dissolved in the RTILs from air and often accompanies water. Since this molecule is electroactive, its removal is required before any electrochemical measurements and can be easily accomplished with extensive argon bubbling.<sup>126</sup> Apart from water, halide impurities are also of main concern when interpreting voltammetric responses. These impurities are generally introduced during the preparation of the ionic liquids, which commonly involves a halide precursor, mainly a chloride or a bromide salt. Seddon et al. showed that presence of chloride led to a substantial increase of viscosity, even at low concentrations.<sup>122</sup> Moreover, chloride and bromide can be easily oxidized at rather low potentials and interfere with the electrochemical process under investigation.<sup>127–129</sup> However, benefit could be derived from this oxidation process of chloride (or bromide). Electrochemical determination of chloride impurity content then can be accurately achieved, while electrolysis can be used to oxidize chloride or bromide to eliminate them from the ionic liquids.<sup>127–129</sup>

### 3.6. Electrochemical Windows

A general common feature of RTILs is their inherent redox-robustness, because of the robustness of the cations and anions employed for their preparation. RTILs generally exhibit a wide potential window, which is a highly desirable property for applying the RTILs as electrochemical solvents. Typical windows of 4.5–5 V have been reported for the RTILs,<sup>31,35,50,51,56,130</sup> and even an enlarged electrochemical window, up to 7 V, was found for [BMIm][BF<sub>4</sub>] and [BMIm][PF<sub>6</sub>] by Gonçalves et al.<sup>130</sup> On the whole, this potential window range is equal to slightly wider than that observed in conventional organic electrolytes but largely exceeds that accessible in aqueous electrolytes. It has been shown that the oxidation of the anions and the reduction of the cations, respectively, are responsible for the anodic and



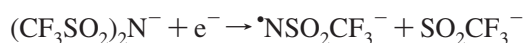
**Scheme 2. Proposed Electrochemical Reduction of Imidazolium Cation According to Ref 130**

cathodic limits observed in the ionic liquids.<sup>31,35,50,56,127,130–132</sup> The potentials at which these processes start determine the accessible electrochemical window. However, an accurate comparison of the various potential windows reported throughout the literature data is difficult. First, as seen in the preceding section, the purity of the ionic liquids has a great influence on the width of the electrochemical window. Second, the nature of the material that is used for the working electrode may modify the decomposition potentials of the electrolyte. Thus, the electrochemical window of 1-butyl-3-methylimidazolium trifluoroacetate, [BMIm][CF<sub>3</sub>COO], is reported to be shorter with platinum than with glassy carbon, probably due to catalytic activity of the platinum metal.<sup>130</sup> Third, the potentials values are often referred against different quasi-references, and consequently, the data cannot be compared with a high level of accuracy.

However, general trends can be brought out. Quaternary ammonium and pyrrolidinium salts are reported to be more stable toward reduction than the corresponding imidazolium salts, due to the improvement of cathodic stability of ammonium and pyrrolidinium cations.<sup>31,50,51,56</sup> The reduction of the imidazolium cation is related to the “high” acidity of the C<sub>2</sub>–H proton (Scheme 2), the reduction of 1,3-dialkylimidazolium cation leading to the formation of a carbene.<sup>31,130</sup> Accordingly, 1,3-dialkyl-2-methylimidazolium, exhibiting a weaker acidity, gave rise to more negative reduction potentials.<sup>31</sup> Johnson and Xiao showed that [BMIm] cation underwent dimerization and dealkylation reactions at the cathode after reduction to the carbene.<sup>127</sup>

By comparing [NTf<sub>2</sub>] salts, MacFarlane et al. noticed that pyrrolidinium salts extended their cathodic limit by 0.5 V with respect to the corresponding quaternary ammonium salts.<sup>50</sup> This electrochemical window is one of the widest ever reported for RTILs. Comparable large electrochemical stability was also observed by Buzzeo et al. for tris[(*N*-hexyl)-tetradecyl]-phosphonium trifluoro-tris(pentafluoroethyl)-phosphate.<sup>133</sup>

On the oxidative side, ionic liquids take advantage of the very stable fluoroanions, such as PF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>, or NTf<sub>2</sub><sup>−</sup>. However, BF<sub>4</sub><sup>−</sup> in [BMIm][BF<sub>4</sub>] was found to decompose into BF<sub>3</sub> and fluorocarbons at the anode.<sup>127</sup> In addition, [PF<sub>6</sub>] and [BF<sub>4</sub>] anions are susceptible to hydrolysis, which may release toxic hydrogen fluoride. In this context, [NTf<sub>2</sub>] is set as a strongly robust anion and has become widely used. But, very recent work clearly suggests that the [NTf<sub>2</sub>] anion engages in a series of reductive reactions beginning at approximately −2.0 V vs Fc/Fc<sup>+</sup>, well before the usually reported cathodic limit.<sup>134</sup> The process is shown to cause cleavage of a S–N bond in the anion.<sup>134</sup>



A less widely used anion, trifluoro-tris(pentafluoroethyl)-phosphate, [FAP], was suggested to allow a substantial improvement of the anodic limit.<sup>133</sup> On the other hand, the wide available electrochemical window provided by the ionic liquids was also suggested to be exploited in molecular

solvents to extend the corresponding potential window.<sup>35,133</sup> A careful analysis of such RTIL/organic solvent system potentialities has been undertaken and concluded that this combination provided an advantage over the commonly used tetrabutylammonium perchlorate/acetonitrile electrolyte with regard to extending the anodic limit but no improvement on the cathodic side.<sup>133</sup>

## 4. Methodological Aspects. Fundamentals and Techniques

Transient and stationary electrochemical methods are commonly used for fundamental knowledge of processes occurring at the electrode/solution interface or in solution when the homogeneous step is triggered by the electron transfer at the electrode. It appeared that the same electrochemical tools could be applied to the ionic liquids for both understanding the properties of the media and studying the species dissolved in the RTILs. However, if the passage from the organic solvent to the ionic liquid has some attractive possibilities, this approach requires taking into account the specificities of the ionic liquid media both inside the solution and at the new type of interfaces.

### 4.1. Electrochemical Methods in RTILs

The properties of ionic liquids (conductivities, solubility of molecules, viscosity) allow classical electrochemical methods to be employed as one could do in organic solvents. As explained in the preceding parts, the basic use of classical electrochemical techniques has been largely reported for investigating the properties of interfaces or molecules dissolved in the RTILs, while the use of fine criteria for analyzing the electrochemical reactivities has been less developed. The most used method for reactivities investigations in RTILs is certainly the cyclic voltammetry. The technique could be used almost as in an organic solvent with special attention about ohmic drop or the value of the diffusion coefficient (see text below). Besides cyclic voltammetry, chronoamperometry and steady-state voltammetry at the microelectrode were used with success to characterize the diffusion transports. Experiments on microdisk electrodes were performed in [BMIm][NTf<sub>2</sub>].<sup>135</sup> The advantage of using a microdisk electrode is the possibility to evaluate both the diffusion coefficient, *D*, and the number of electrons associated with the electrode reaction using the passage from a linear to a spherical diffusion. The one-electron and two-electron reductions of some typical organic compounds (nitrobenzene, nitrophenol, naphthoquinone, chloranile, 9,10-phenanthrenequinone) were examined in the ionic liquid, allowing the determination of both *n* and *D* according to Shoup and Szabo.<sup>136</sup>

As with the other steady-state methods, hydrodynamic methods were also considered because of their advantage of not suffering capacitive charging current. Osteryoung et al. have reported the study of rotating disk voltammetry for ferrocene in RTILs.<sup>137</sup> High-speed channel electrode voltammetry was employed for investigations in the less viscous RTILs and allowed the measurements of the heterogeneous electron transfer rates.<sup>138</sup> This steady-state method uses high flow rates over a microband electrode obtained by pressurizing a chamber containing the ionic liquid.

Scanning electrochemical microscopy (SECM) was tested in [BMIm][BF<sub>4</sub>] using the ferrocene as mediator.<sup>139</sup> Despite some limitations, SECM provides interesting possibilities for

probing ionic liquid–substrate interfaces or ionic liquid–interface between two immiscible electrolyte solutions (ITIES) interfaces.<sup>140,141</sup> Approach curves revealed that steady-state SECM could be achieved by considering some special conditions (small electrodes, low approach rate). Electrochemical imaging with SECM in RTILs is possible. This possibility was illustrated with the case of a Ag disk substrate in contact with the ionic liquid media.<sup>139</sup> SECM was also used with dioxygen as mediator to analyze the transport properties of small charged species in ionic liquids.<sup>75</sup>

As a complement to purely liquid methods, solid-state voltammetry in ionic liquids where nanoparticles are deposited on an electrode surface was developed for the investigation of insoluble redox systems (see section 5.5).<sup>142</sup>

#### 4.1.1. References Electrodes

One of the technical difficulties to obtain reliable electrochemical measurements in the RTILs arose from the lack of established reference electrodes. It is particularly important to control and measure the electrode potential against a reference electrode, the potential of which is stable and reproducible during experiments. The difficulties involved in comparing potential values in the absence of true absolute reference electrodes are related to junction potentials and/or subtle activity differences. To date, voltammetric measurements have mainly employed quasi-reference electrodes, mostly platinum or silver wires. This practice, although convenient, cannot allow comparison of the data with those obtained in conventional electrolytes. Less commonly, the  $I^-/I_3^-$  redox couple,<sup>31</sup> the  $Li^+/Li$  couple,<sup>143</sup> and platinum wire coated with polypyrrole<sup>67,144</sup> have been also used as reference electrode systems in the RTILs. To circumvent the difficulties of comparisons between the different potential references, Bond and co-workers recommend the use of metallocene derivatives as reference standard compounds.<sup>145</sup> In [BMIm][PF<sub>6</sub>], the reversible one-electron reduction of cobaltocene was found to be independent of electrode composition, concentration, and scan rate. Similar results were obtained with the reversible one-electron oxidation of ferrocene, although this well-known electrochemical standard was reported to be poorly soluble in [BMIm][PF<sub>6</sub>].<sup>145</sup> Because the ferrocene/ferricenium couple has been described as a stable, well-defined redox system in many ionic liquids and was already employed as internal probe in many studies in conventional electrolytes, it practically becomes the most widely used reference standard in the RTILs. More recently, Compton and co-workers advocated the use of the TMPD/TMPD<sup>•+</sup> system (where TMPD = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine) as a highly suitable redox couple for use in reference electrodes for ionic liquids.<sup>146</sup>

However, several attempts have been made to build “true” reference electrodes.<sup>126,147–149</sup> A Ag<sup>+</sup>/Ag reference electrode, with the silver salt dissolved in [EMIm][NTf<sub>2</sub>], was reported.<sup>126</sup> But, this report suffered from a lack of data regarding the stability of this electrode to fully evaluate its performance as a reference. References electrodes based on Ag/Ag<sup>+</sup> couple or Ag/AgCl were also proposed.<sup>147</sup> In those systems, the redox couples are always in contact with a soluble salt, AgNO<sub>3</sub> and Bu<sub>4</sub>NCl, respectively, and the salts, first dissolved in acetonitrile, are added to the ionic liquid of choice. While stability measurements fulfilled the criteria required for reference electrodes, loss of acetonitrile is likely to arise after several days of use at ambient temperature.<sup>147</sup>

A Ag<sup>+</sup>/Ag reference electrode consisting of a silver wire immersed in a solution of silver trifluoromethanesulfonate in [Pyr<sub>4</sub>][NTf<sub>2</sub>] was tested in terms of stability and reproducibility.<sup>148</sup> The voltammetric monitoring of the ferrocene and cobaltocenium redox potentials have shown that this system is stable, within 1 mV, over a lifetime of 3 weeks.<sup>148</sup>

#### 4.1.2. Difficulties Related to Transport and Ohmic Drop in RTILs

Conductivities of ionic liquids suggest that there are no real difficulties to compensate the residual ohmic drop as classically achieved in transient electrochemical methods. In other words, the standard equipment used in electrochemistry<sup>150</sup> is directly usable to perform the experiments in RTILs. However, to limit the interference of the residual ohmic drop with experimental measurements due to the working electrode resistance, special care has to be taken in order to compensate the residual ohmic drop due to working electrode resistance, especially for the highest scan rates ( $> 50 \text{ V s}^{-1}$ ). On a 1 mm diameter disk electrode, typical resistances were reported to range between 4.5 and 5.5, 2.5 and 3.5, 5 and 6, and 24 and 28 k $\Omega$  for [BMIm][NTf<sub>2</sub>], [EMIm][NTf<sub>2</sub>], [BMIm][PF<sub>6</sub>], and [Me<sub>3</sub>OctN][NTf<sub>2</sub>], respectively.<sup>67</sup> These values could be compared with those of conventional electrolytic media such as acetonitrile/Bu<sub>4</sub>NBF<sub>4</sub>, which are in the range of 0.4–0.8 k $\Omega$ . The resistance values reported with imidazolium-based ionic liquids are low enough to be fully compensated by classical equipment, whereas the higher resistance values obtained in a more resistant ionic liquid, for example, [Me<sub>3</sub>OctN][NTf<sub>2</sub>], make detailed mechanistic studies in this latter medium somewhat more difficult. As already mentioned for other properties of ionic liquids, one should remember that all these resistance values are highly dependent on the amount of residual water present in the ionic liquid.

#### 4.1.3. The Diffusion Coefficients Problem

As explained previously, diffusion coefficients in ionic liquids are smaller than those in conventional organic solvents. These low *D* values result in low currents and imply the use of higher solute concentrations to improve the signal-to-noise ratio, becoming a problem when the solubility of the molecule is low in the RTILs.

For stationary methods using an ultramicroelectrode, low diffusion rates also result in longer time for reaching steady-state conditions.<sup>135</sup> The competition between the linear diffusion, for which peak-shaped voltammograms are obtained, and the spherical diffusion, for which S-shaped voltammograms are obtained, depends on a simple parameter  $p = [(RT)/(Fv)](D/r^2)$  where *R* is the gas constant, *D* the diffusion coefficient, *F* the Faraday constant, *r* the radius of the ultramicroelectrode, and *v* the scan rate.<sup>151</sup> It results that microelectrodes, with smaller diameter, are generally required for the more viscous RTILs. In terms of practical use (for example, to extract “diffusion-limiting current” from stationary voltammograms), it also means that very slow scan rates have to be used to achieve the spherical diffusion conditions. As pointed out by Osteryoung et al.,<sup>137</sup> obtaining true steady-state limiting current in RTILs is far from trivial. The authors recommend using slow scan rates in both rotating ring-disk electrode and microelectrode voltammetry, steady-state being only achieved at 10 mV s<sup>−1</sup> or below for a 5  $\mu\text{m}$  radius disk.<sup>65,137</sup> Microelectrodes can give rise to transient-like

voltammograms that are peak-shaped, even at modest scan rates. Moreover, when one attempts to reach diffusional steady state current, the influence of the natural convection has to be taken into account. This phenomenon, which is well-known in conventional media,<sup>152,153</sup> is of special importance when the diffusion mass transfer is low, as in ionic liquids. It results in S-shaped voltammograms but ones containing artifacts, such as higher limiting plateau currents. The notion of natural convection in ionic liquid is not clear, but qualitatively, the phenomenon is likely to be a problem with the more viscous ionic liquids, where  $D$  values are small, and with the common size microelectrode (5–10  $\mu\text{m}$  radius). Indeed, consequences have already been detected in steady-state experiments on microelectrodes.<sup>75</sup>

Besides these expected difficulties, another point that is rarely a problem in electrochemical methods arises from the special solvation of charged molecules by the ions of the RTILs. This “ionic solvation” induces considerable variations of the molecules’ transport properties in ionic liquids when the charge of a molecule is modified consecutively to an electron transfer. As set out in section 3.3, it results that the diffusion coefficients of the oxidized and reduced forms of a redox couple could be very different in RTILs, contrary to the case of organic solvents where this phenomenon is generally negligible. The consequences of the inequality of diffusion coefficients on electrochemical measurements are complex and sometimes difficult to detect but could affect the derived values as redox potentials or other kinetic measurements. Indeed, measurements of electrochemical kinetics are generally based on a competition between the diffusion rate of electroactive species to the electrode and the reaction of interest, meaning that anomalies on the diffusion rates will induce error on the final measurement.<sup>151</sup>

To date, the most spectacular effect related to this phenomenon was evidenced by Compton et al. with the reduction of dioxygen to the superoxide in two different common ionic liquids.<sup>74</sup> Cyclic voltammetry at ultramicroelectrodes directly demonstrated that the inequality of the diffusion coefficients created changes in the diffusion regime, having strong repercussions on the voltammetric response.<sup>74</sup> More recently, the same redox couple  $\text{O}_2/\text{O}_2^{\bullet-}$  was used as a mediator in scanning electrochemical microscopy (SECM).<sup>75</sup> As expected, the inequalities of the diffusion coefficients lead to large anomalies in the current responses, which, in extreme cases, impede the recording of stationary approach curves. However, this difficulty can be transformed in a very elegant method for estimating these inequalities. This approach was illustrated using [BMIm][NTf<sub>2</sub>] and [Et<sub>3</sub>BuN][NTf<sub>2</sub>] salts. The current–time SECM curves allowed the determination of the diffusion coefficients of the oxygen, as well as the diffusion coefficients of the superoxide, and the obtained results confirm the huge difference between diffusion coefficients (by a ratio of 10–30) of oxygen and electrogenerated superoxide in the ionic liquids.<sup>75</sup>

## 4.2. RTIL/Electrode Interface

Basic investigations of solvent/metal interface generally involve capacitance measurements since the method provides a simple way for investigating the solvent at the interface. However, the literature data concerning capacity measurement with RTILs is essentially limited to a single paper.<sup>154</sup> Specific capacitances at the electrode/electrolyte interface at glassy carbon or mercury electrodes and RTILs were investigated with [EMIm] as cation and four different anions.

Capacitance values in the range 11–12  $\mu\text{F cm}^{-2}$  were reported for carbon and Hg electrodes. However, much controversy accompanies the physical interpretation of these experimental measurements, typically capacitance–potential curves in RTILs.<sup>155</sup> Several anomalies have been reported that cannot be explained by the Gouy–Chapman theory. For example, the zero charge potential obtained from the electrocapillary maximum does not correspond to the capacitance minimum. But, all these results are not surprising since the application of the dilute-solution approximation, which is the settlement of the Gouy–Chapman theory, is unjustified in these highly ion-concentrated media.<sup>155</sup>

Concerning other relevant experimental investigations about nonhaloaluminate RTILs, by focusing on the description of the interface structure, most of studies were based on spectroscopic methods and illustrated the complexity of the system. X-ray measurements on thin films on Si(111) surface with 1-alkyl-3-methylimidazolium salts in the liquid show their ability to form organized layers at solid interfaces.<sup>156</sup> First measurements of the composition and molecular orientation at a liquid surface in vacuum of [BMIm][PF<sub>6</sub>], using time-of-flight ion scattering and recoil spectroscopy, showed that no ion was significantly enriched in the surface. The average orientation of the cation was found to be with the plane of the imidazolium ring vertical to the surface.<sup>157</sup> Concerning the interface with a metal, the molecular structure of [EMIm][BF<sub>4</sub>] at a gold electrode was later investigated by means of *in situ* FT-IR as a function of the potential applied to the electrode. The FT-IR spectra suggested a different arrangement for [EMIm] cation present at the metal interface. The imidazolium cation oriented vertically in a potential range of –1.3 to +0.6 V vs Ag/Ag<sup>+</sup>.<sup>158</sup> More recently, sum frequency generation (SFG) experiments performed with similar RTILs, [BMIm][PF<sub>6</sub>] or [BF<sub>4</sub>], found a different orientation. The SFG spectra indicate that the cation modifies its orientation at the electrode when the potential at the electrode changes. The plane of the imidazolium rings tips from 35° at positive surface charge to around 60° from the surface normal at negative surface charge. Moreover, the orientation changes of the cation with the potential were found to be dependent on the anion and substrate nature.<sup>159,160</sup> The solvation force profile for [EMIm][AcO] on graphite has been measured using atomic force microscopy. For this type of surface, the imidazolium cation was found to adopt a flat orientation relative to this substrate that is ascribed to favorable interactions between the alkyl backbone of the cation and the substrate.<sup>160</sup>

Despite the lack of experimental data, different approaches were proposed to model the electrochemical interface. Some of them were devoted to reconstruction or adaptation of the Gouy–Chapman theory, and limits of this approach were recently discussed.<sup>155</sup> The problem remains complex because the behavior of ionic liquids near charged surfaces differs from that of dilute electrolytes. The hypothesis used for dilute solution, where ions are considered as point charges as a first approximation with size effects as secondary consideration leading to the double layer model, was found to be not valid. Using molecular dynamics, simulation of an electroactive interface allows quantitative description of the ionic liquid interface, especially concerning the dependence of the capacitances on the applied potential.<sup>161</sup> In RTILs, the ions are in close contact, so their sizes and shapes are of primary importance. This leads to charge oscillation that may penetrate quite deeply into the liquid and required specific



simulation of the considered RTILs.<sup>162</sup> [BMIm][Cl] was recently simulated using molecular dynamics for increasing electric field, and a systematic rearrangement of the ions was observed mainly due to the anion segregation toward the positive electrode.<sup>163</sup> However, in the present day, there is a clear lack of a completed model that should allow treatment of the electron transfer process and proposal of a kind of Frumkin correction when the electron transfer rate constant at the electrode surface is measured. For example, the ability of imidazolium-based RTILs to form organized layer at the interface may have a special influence on the apparent electron transfer kinetics as proposed to explain some experimental kinetic measurements on these systems.<sup>67,138,164,165</sup>

## 5. Molecular Electrochemistry - Electrochemical Behavior in Ionic Liquids

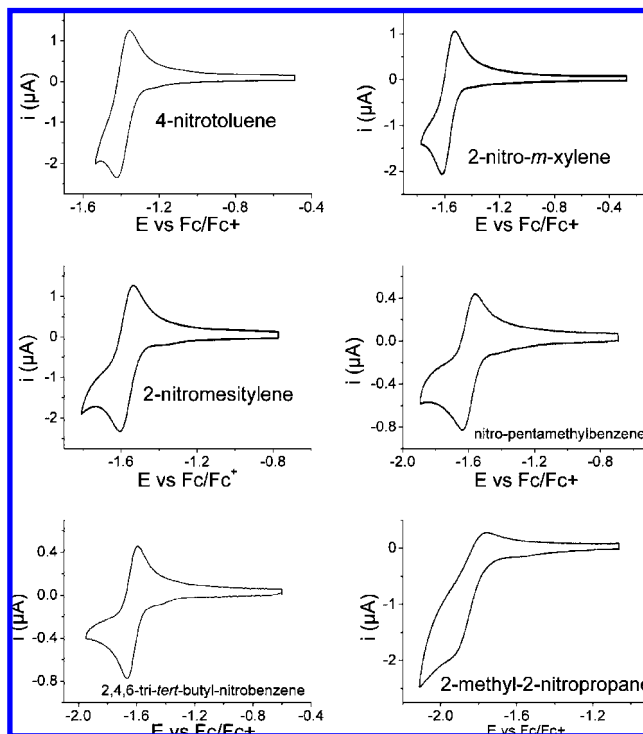
### 5.1. Electrochemical Mechanism: Fundamental Analysis

#### 5.1.1. Simplest Investigations: Reversible Systems

The first reported investigations were related to the oxidation or reduction of one-electron reversible couples, for which the initial purpose was to compare the voltammetric response of simple electrochemical systems with their corresponding behaviors in organic solvents. The main part of these works concerns the comparison between the diffusion coefficients in RTILs and in classical solvent. Ferrocene, cobaltocene, or tetrathiafulvalene in common RTILs, [BMIm][PF<sub>6</sub>] and [EMI][BF<sub>4</sub>], were investigated, showing the same general patterns in RTILs as those in molecular solvent containing an electrolyte.<sup>63,137,145</sup> Later, cyclic voltammetry experiments of the oxidation of ferrocene to ferricenium (Fc/Fc<sup>+</sup>) in RTILs were completed by using a large range of scan rates (typically from 0.1 V·s<sup>-1</sup> to 1000 V·s<sup>-1</sup>) and confirmed that well-defined waves were observed for the whole range of scan rates.<sup>67</sup> In all these ionic liquids, the peak currents for the reduction/oxidation of ferrocene were found to vary linearly with the square root of the scan rate, showing that the electrochemical process is diffusion-controlled.<sup>67,70,71</sup> In common RTILs, the Fc/Fc<sup>+</sup> couple is electrochemically reversible with small peak-potential differences ( $\Delta E$ ) between the forward and backward scans (typically 57 and 73 mV at scan rates of 0.1 and 1000 V·s<sup>-1</sup>, respectively), which corresponds to a relatively fast electron-transfer kinetics. The standard potentials,  $E^\circ$ 's, were classically derived from the half-sum between the forward and reverse peak potentials. In this case, it was considered that half-wave potentials,  $E_{1/2}$ , are close to the standard potentials  $E^\circ$ , neglecting the possible difference on  $D$  coefficients between the neutral and charged species ( $E_{1/2} = E^\circ + RT/(2F) \ln(D_i/D_o)$ ).

#### 5.1.2. Electron Transfer Thermodynamic and Kinetic Analyses

The evolution of the reactivity is a major question when a reaction is transferred from a conventional organic medium to an ionic liquid. This has led several authors to use electrochemical methods for investigating how model electrochemical reactions are going to be affected by ionic liquids. If a significant amount of work was dedicated to diffusion coefficients measurements, there are less fundamental investigations taking a deal of interest in how electron



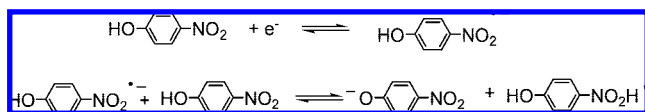
**Figure 1.** Cyclic voltammetry in ionic liquids, reduction of nitro compounds on a glassy carbon electrode. Scan rate = 0.2 V s<sup>-1</sup>. All voltammograms were recorded in [BMIm][NTf<sub>2</sub>] except for the 2,4,6-tri-*tert*-butyl-nitrobenzene, which is in [Et<sub>3</sub>BuN][NTf<sub>2</sub>]. Reprinted with permission from ref 166. Copyright 2005 Elsevier.

transfer kinetics would be modified by the ionic liquids. In this context, investigations focused both on the thermodynamics ( $E^\circ$  measurements) and the kinetics through the measurement of apparent heterogeneous standard electron-transfer rate constants,  $k_s$ . Investigations can be separated into two categories depending on the charge carried by the electrogenerated species (positive or negative).

About the properties of a radical anion and thus the possible interactions with the cation of the ionic liquid, a series of substituted nitrobenzene and an aliphatic nitro compound was studied both in acetonitrile and in [BMIm][NTf<sub>2</sub>] and [Et<sub>3</sub>BuN][NTf<sub>2</sub>] using cyclic voltammetry.<sup>166</sup> As found for the metallocenes, the general electrochemical patterns for the reduction of NO<sub>2</sub> compounds in RTILs were not too different from the well-known behavior reported in organic solvents.<sup>166,167</sup> These molecules display chemically reversible monoelectronic voltammograms (Figure 1).

On the whole, the same and expected relative trends for the variation of the  $E^\circ$ 's with the molecule structure were found in the RTILs and in acetonitrile. For example,  $E^\circ$ 's become more and more negative when donor groups are introduced on the aromatic ring. These basic observations show that the same electrogenerated radical anions are produced in both RTILs and ACN and that their lifetimes were not considerably affected. A similar behavior was reported for the reduction of the unsubstituted nitrobenzene, which is reversibly reduced by one electron and further by two electrons in a chemically irreversible step.<sup>167</sup> In the same work, the authors have also examined the more complicated reduction of nitrophenol, revealing three reductive steps (two irreversible and one reversible) that were ascribed to the existence of the self-protonation mechanism as already



**Scheme 3. Mechanism for the Reduction of Nitrophenol in Ref 167**

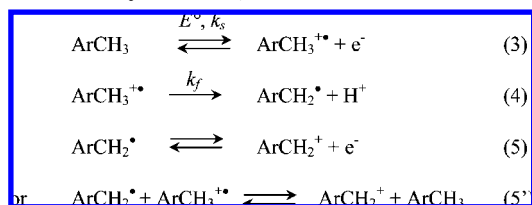
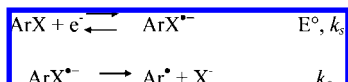
reported in organic solvents where the key step is the reaction between the radical anion and another nitrophenol molecule acting as a proton donor (Scheme 3).<sup>167</sup>

As a general tendency for nitro aromatic compounds, the  $E^\circ$ 's are always less negative in the ionic liquid than in ACN/ $\text{NBu}_4\text{PF}_6$  as an electrolyte.<sup>166,168–170</sup> All potentials are positively shifted by 100–110 mV when they pass from ACN to  $[\text{Et}_3\text{BuN}][\text{NTf}_2]$  and around 240–260 mV when they pass from ACN to  $[\text{BMIm}][\text{NTf}_2]$ .<sup>166</sup> This shift corresponds to a higher stabilization of the electrogenerated radical anion by the cation of the ionic liquid through ion-pairing associations. The stabilization was found to be higher when the ionic salt contains an imidazolium cation rather than a bulky ammonium cation. In simple electrostatic considerations, the ion-pairing stabilization should be dependent on both the distance between the RTIL cation and the  $\text{NO}_2$  radical anion and the charge density. In the radical anion, a large part of the negative charge is localized on the nitro group, and thus a relevant distance is the distance between the  $\text{NO}_2$  group and the cation. The stronger interactions with  $[\text{BMIm}]$  can be explained by a lower distance between the charge center of the radical anion and the cation due to the planar geometry of the imidazolium ring and by the ability of the imidazolium cation  $[\text{BMIm}]$  to make hydrogen bonds.<sup>166</sup> This interaction between negatively charged species and the cation leads to spectacular effects when more than one charge is introduced in the molecules.<sup>168</sup> Indeed, 1,4- and 1,2-dinitrobenzenes exhibit two one-electron processes in acetonitrile (with a quaternary ammonium salt as electrolyte) but a single two-electron reversible process in  $[\text{BMIm}][\text{BF}_4]$ .<sup>168</sup> This effect is due to strong ion pairing between the imidazolium cation and the dinitrobenzene dianion, which demonstrates the unusual ion-pairing properties of these media. However, the existence of a strong interaction between the charged species and the cation is extremely sensitive to the cation structure and its influence may vary to a large extent. Recently, the reductive electrochemistry of a family of substituted benzophenones was investigated in  $[\text{BMIm}][\text{NTf}_2]$  and  $[\text{Pyr}_4][\text{NTf}_2]$ .<sup>169</sup> In this last RTIL, two well-defined one-electron processes were observed, corresponding to the reversible formation of the radical anion and dianion of benzophenone. The second reversible process was found to be 0.62 V more negative than the first one, which is around the values found in molecular solvents, suggesting that the strength of ion-pairing interaction is low in this RTIL. In contrast, for the same experiment performed in  $[\text{BMIm}][\text{NTf}_2]$ , the authors observed at low scan rates irreversible processes. The difference of potentials for the formation of the radical anion and the dianion was on the order of 0.15–0.17 V, indicating much stronger interactions of the electrogenerated species with the imidazolium cation.<sup>169</sup> Similarly, the reduction of benzaldehyde was studied in two ionic liquids ( $[\text{BMIm}][\text{NTf}_2]$  and  $[\text{Pyr}_4][\text{NTf}_2]$ ) that display similar viscosities.<sup>164</sup> In both RTILs, the electrochemical reduction occurs via classical two sequential one-electron processes, leading to the production of the radical anion followed by its corresponding dianion species. Reduction potentials in  $[\text{BMIm}][\text{NTf}_2]$  were found to be shifted

anodically relative to those in  $[\text{Pyr}_4][\text{NTf}_2]$ , which indicates a stronger interaction between the cation of the RTIL and the radical anion and dianion of the benzaldehyde.<sup>164</sup>

About the kinetics of electron transfer, the standard heterogeneous rate constants,  $k_s$ , were measured assuming that the Butler–Volmer law is valid and that the diffusion coefficients are equal for the reduced and oxidized species of the redox couple. The  $k_s$  values were generally derived from classical cyclic voltammetry measurements based on the variation of  $\Delta E_p$  (difference between the anodic and the cathodic peak potentials) with the scan rate or from steady-state methods. As explained previously, the lack of knowledge of the metal–RTIL interface makes difficult any correction for effect of the interface. Thus, for both oxidation and reduction investigations, only apparent  $k_s$  values were determined without correction from the double layer effect and investigations focused on the relative effect for a given compound and a given electrode.<sup>138,164–166</sup> By taking into account these limitations, the derived  $k_s$  values were determined for the formation of radical anion and were generally found to be significantly lower in ionic liquids than in a molecular solvent. Depending on the RTIL and on the molecule structure, large decreases were observed as for the reduction of several aromatic nitro compounds that is considerably affected by the passage from the ACN to  $[\text{BMIm}][\text{NTf}_2]$  or  $[\text{Et}_3\text{BuN}][\text{NTf}_2]$  (by a ratio 10–100). For example, the nitrotoluene reduction is fast in acetonitrile ( $k_s > 1 \text{ cm s}^{-1}$ ) and becomes sluggish in the  $[\text{Et}_3\text{BuN}][\text{NTf}_2]$  ( $k_s \approx 0.01 \text{ cm s}^{-1}$ ). Similarly, for the reduction of benzaldehyde in  $[\text{BMIm}][\text{NTf}_2]$ , similar effects to those reported for the reduction of nitro compounds were detected, that is, a large decrease of the heterogeneous electron transfer rate constant by comparison with classical molecular solvent.<sup>164</sup> In contrast, in  $[\text{Pyr}_4][\text{NTf}_2]$ , the electron transfer kinetics for the same redox couple was found to be similar to that measured in a noninteracting molecular solvent containing quaternary ammonium electrolytes. This difference of behavior observed between these two types of ionic liquids suggests more complex interactions than simple electrostatic ion pairing, which could also involve  $\pi$ – $\pi$  interactions or H-bonding that are possible with imidazolium and not possible with pyrrolidinium cations. To explain the lower kinetics, the same authors suggested that ordering in the RTIL may play a role in the kinetics slowing. Ordering would lead to higher solvent reorganization and slower double-layer interface relaxation, which would both result in apparent slow heterogeneous kinetics.<sup>164</sup>

Concerning the behavior of positively charged species that could reflect the interactions of the electrogenerated species with the anion of the RTILs, the oxidations of ferrocene compounds were the most detailed investigated systems. A series of ferrocene derivatives were studied in different RTILs and heterogeneous electron-transfer rates were measured under steady-state conditions.<sup>138</sup> In imidazolium-based RTILs, electron transfer rate constants,  $k_s$ , were found to be lower by comparison with the same values determined in acetonitrile as reported for the radical anions. However, no correlation was found between the size of the molecules estimated from the hydrodynamic radius in the RTILs and the heterogeneous electron transfer rate constants, indicating that other factors operate. Concerning the ferrocene oxidation, temperature dependencies of the electron transfer kinetics and of the diffusion coefficients for the ferrocene/ferricenium were investigated in  $[\text{Et}_3\text{HexN}][\text{NTf}_2]$ . The kinetic rate

**Scheme 4. Proposed ECE-DISP1 Mechanism for the Oxidation of Alkylbenzenes, ref 67****Scheme 5. Generally Acknowledged Mechanism for the Reduction of Halogenoaromatic Compounds**

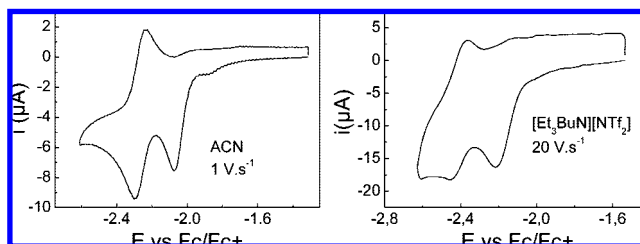
constants were found to be slower than those in molecular solvent, and both the  $k_s$  and  $D$  increase monotonously with the temperature, although these two values are not correlated.<sup>171</sup> In a detailed investigation of the oxidation of the *para*-toluidine in [Pyr<sub>4</sub>][NTf<sub>2</sub>], the authors reported a value of  $k_s$  1 order of magnitude lower than that observed for the oxidation of this molecule in ACN.<sup>165</sup> It is notable that in the same RTIL, [Pyr<sub>4</sub>][NTf<sub>2</sub>], for a reduction process, that is, the reduction of benzaldehyde to its radical anion, no considerable variation of the kinetics of the electron transfer was observed between a molecular solvent and the RTIL.<sup>164</sup> This difference illustrates the special role played by the anion and the cation in the same RTILs and the precautions that have to be taken before drawing general conclusions.

**5.2. Reactivity Associated with the Electron Transfer**

Electron-transfer processes involving homogeneous chemical reactions, especially those with aromatic hydrocarbons, have been widely studied in molecular electrochemistry since the resulting radical cations or anions participate in a large variety of reactions. These reactions were the subject of recent studies to appreciate the effects of RTILs on the reactivity of radical ions.<sup>67,172</sup> Some structural effects such as those obtained by changing the size of the molecule or the localization of the injected charge were more particularly investigated. Despite the difference between ionic liquids and molecular solvents, it is notable that the criteria classically used in electrochemical analysis, such as the variation of the peak potential or its intensity with the scan rate in cyclic voltammetry, remain valid in the RTILs.

**5.2.1. Reactivity of Aromatic Hydrocarbon Radical Cations in Ionic Liquids**

Oxidation of aromatic hydrocarbons of different sizes (naphthalene, anthracene, durene) to their radical cations were investigated in imidazolium- and quaternary ammonium-based RTILs using high scan-rate voltammetry up to 10 000 V s<sup>-1</sup>.<sup>67</sup> For all the investigated systems, diffusion-controlled electrochemical processes were observed as attested by the variations of the peak current with the square root of the scan rate. Lifetimes of the produced radical cation were estimated in the RTILs by simply looking at the scan rate required for observing the appearance of the reversibility. The reversibility was detected for anthracene at 2000–3000 V s<sup>-1</sup> in [BMIm][NTf<sub>2</sub>] but was not observed for naphthalene. Same results are commonly observed in molecular solvents, where the reactivity of the radical cation of a



**Figure 2.** Cyclic voltammograms of the reduction of ClAnt ( $2 \times 10^{-3}$  mol L<sup>-1</sup>) in ACN (with 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NBF<sub>4</sub>) and ClAnt ( $\approx 1 \times 10^{-2}$  mol L<sup>-1</sup>) in [Et<sub>3</sub>BuN][NTf<sub>2</sub>] at different scan rates on a 0.5 mm glassy carbon disk. Reprinted with permission from ref 174. Copyright 2004 American Chemical Society.

polyaromatic hydrocarbon is known to decrease with the size of the aromatic hydrocarbon.<sup>67</sup>

Less delocalized cation radicals of alkylbenzenes, like the one obtained from durene, are known to display a different reactivity due to the C–H<sup>+</sup> acidity, and the deprotonation from the cation radical is the predominant type of decay. Similar behavior was found in [BMIm][NTf<sub>2</sub>] where the nature of the electrochemical mechanism was found to follow the same ECE-DISP1 mechanism as that in ACN (Scheme 4).<sup>67</sup>

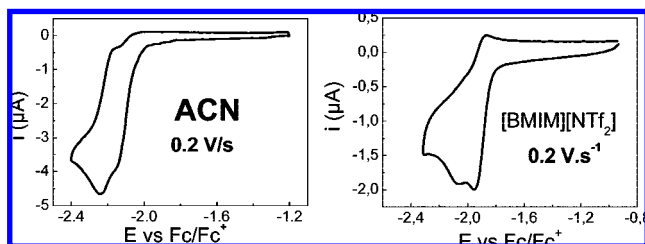
Estimations of  $k_f$  in [BMIm][NTf<sub>2</sub>] or in [EMIm][NTf<sub>2</sub>] were found to be identical to those measured in ACN (with Et<sub>4</sub>NPF<sub>6</sub>) medium. It shows that for this radical cation, no effect could be evidenced in the kinetics of the consecutive first-order reaction because of the use of RTILs.<sup>67</sup>

**5.2.2. Reactivity of Halogenated Organic Molecules: Carbon–Halogen Cleavage Rates**

**Halogenated Aromatic Compounds.** Bond cleavage reactions are classical processes in organic chemistry. In conventional media, these redox systems involve first the formation of radical anion, followed by the cleavage of the carbon–halogen bond (Scheme 5).

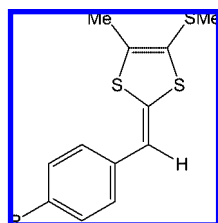
It was previously found that the reactivity of the radical anions can be considerably affected by the media with the presence of interacting cation.<sup>173</sup> Two well-known electrochemical processes were chosen to evaluate the influence of an ionic medium. The electroreductions of 9-chloroanthracene and 4-chlorobenzophenone were investigated in three different RTILs sharing a common anion, [BMIm][NTf<sub>2</sub>], [Me<sub>3</sub>BuN][NTf<sub>2</sub>], and [Et<sub>3</sub>BuN][NTf<sub>2</sub>].<sup>174</sup> The delocalization of the charge in the radical anion is expected to be different, well-delocalized over the aromatic system for the Cl–anthracene radical anion, ClAnt<sup>•-</sup>, and more localized on the C=O group for the benzophenone radical anion, ClBz<sup>•-</sup>. The evolutions of the cleavage reactivity with the media were found to be completely different for the two types of radical anions (see Figures 2 and 3). A small increase of the C–Cl cleavage rate was observed for the 9-chloroanthracene radical anion, whereas a large decrease is found for the 4-chlorobenzophenone radical anion.

These effects were rationalized in terms of specific ion-pair associations between the radical anion and the cation of the ionic liquid that stabilizes the unpaired electron in the  $\pi^*$  orbital of the aromatic system and thus decreases its presence in the  $\sigma^*$  bond breaking. When the negative charge is spread out over the whole molecule as for the 9-chloroanthracene radical anion, the carbon–halogen bond cleavage accelerates due to specific interaction between the cation of the ionic liquid and the small leaving ion. In radical anions,

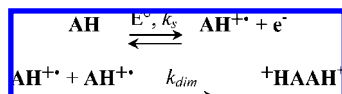


**Figure 3.** Cyclic voltammograms of the reduction of ClBz ( $2 \times 10^{-3}$  mol L $^{-1}$ ) in ACN (with 0.1 mol L $^{-1}$  Bu $_4$ NBF $_4$ ) and ClBz ( $\approx 1 \times 10^{-2}$  mol L $^{-1}$ ) in [BMIM][NTf $_2$ ] at 0.2 V s $^{-1}$  on a 0.5 mm glassy carbon disk. Reprinted with permission from ref 174. Copyright 2004 American Chemical Society.

**Scheme 6.** Structure of 1,4-Dithiafulvene (AH)



**Scheme 7.** RC–RC Coupling Mechanism

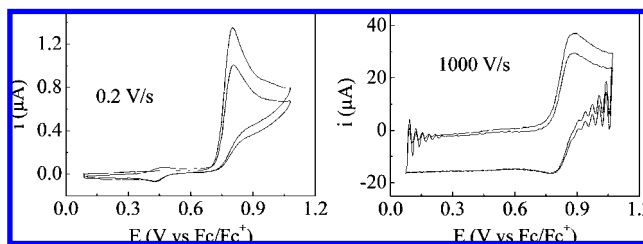


where the negative charge is more concentrated on a small area of the molecule (mostly on the oxygen atom of the carbonyl group), a large decrease of the cleavage reactivity occurs. In this case, the stabilization of the leaving group still exists but is largely overcompensated by the stabilization of the radical anion in agreement with the positive shift of the reduction potential. As explained previously, the ion-pair association stabilizes the  $\pi^*$  orbital where the unpaired electron is located and thus decreases its ability to be transferred into the  $\sigma^*$  of the breaking bond.<sup>174</sup>

**Alkyl Halogenated Compounds.** Very few papers were devoted to the direct electroreduction of halogenated alkanes in RTILs. Reduction potentials for the direct electroreductions of trichloroacetic acid, dichloroacetic acid, dibromoethane, and benzyl chloride were reported as  $-1.91$ ,  $-1.82$ ,  $-1.83$ , and  $-2.05$  V/SCE, respectively, in [BMIm][PF $_6$ ] on an inert electrode material (glassy carbon electrode).<sup>175</sup> More detailed investigations of the direct electroreduction of a series of Freon compounds (CF $_2$ ClCFCl $_2$ , CF $_2$ BrCF $_2$ Br, CF $_2$ BrCFClBr, CF $_2$ BrCFClBr, and of the simple CF $_3$ Br) were reported in [BMIm][NTf $_2$ ], [Pyr $_4$ ][NTf $_2$ ], [BMIm][PF $_6$ ], [Hex $_3$ tetradecylP][NTf $_2$ ].<sup>176</sup> Irreversible but well-defined voltammograms were reported on glassy carbon electrode. For the two first and less viscous RTILs, measured reduction potentials were similar to those reported in DMF. A cathodic shift was observed when the electroreduction was performed in the two other, more viscous RTILs, but the shift was ascribed to uncompensated solution resistance.

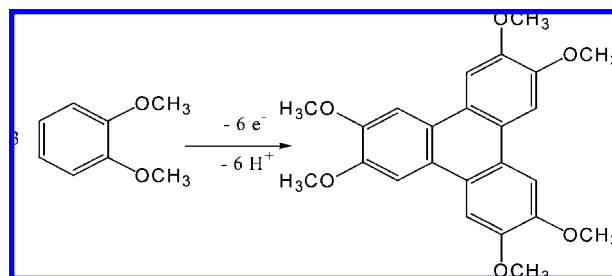
### 5.2.3. Electrodimerization Reactions in Ionic Liquids

Electrodimerization and electropolymerization (that is the occurrence of several electrodimerization steps) represent an important class of reactions involved in the design of organic materials like conducting polymers.<sup>177</sup> Several redox systems, in which a coupling step follows the heterogeneous electron transfer, have already been investigated in common ionic



**Figure 4.** Cyclic voltammograms of  $10^{-2}$  mol L $^{-1}$  of veratrole in [EMIm][NTf $_2$ ] at a platinum electrode (0.3 mm of diameter) recorded at different scan rates. Reprinted with permission from ref 67. Copyright 2003 American Chemical Society.

**Scheme 8.** Electrogeneration of HMT



liquids. No clear general rule has emerged from the reported behaviors in ionic liquid with those known in conventional molecular solvents. The influence of the ionic liquid was found to be very different depending both on the nature of the electrogenerated intermediate and on the cation of the ionic liquid. Mechanistic analyses were essentially based on cyclic voltammetry experiments. Variation of the peak potential with the scan rate, the initial concentration, or both in relation with digital simulations were used allowing it to be established that the same mechanism occurs in organic solvents and in RTILs.<sup>67,164,165,170,178</sup>

### Examples of Oxidative Electrodimerization in RTILs.

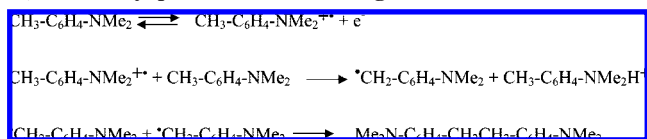
The electrodimerization of a nitro derivative of the 1,4-dithiafulvene (AH) was chosen as a test system (Scheme 6) because this class of molecules was extensively studied in molecular solvent.<sup>179</sup> In these conventional media, the mechanism involves the formation of a radical cation followed by the fast irreversible formation of a dimer ( $^+HAAH^+$ ) from a radical-cation–radical-cation coupling (Scheme 7).

In [BMIm][NTf $_2$ ], [EMIm][NTf $_2$ ], and [BMIm][PF $_6$ ], the 1,4-dithiafulvene displays an irreversible electrochemical system as reported in organic solvent.<sup>179</sup> The oxidation peak potential was found to vary linearly with the log( $v$ ) ( $v$  is the scan rate) between 0.1 and 100 V s $^{-1}$ , with a slope close to 19 mV per decade, which are the values expected for a mechanism in Scheme 7. Measured values of  $k_{dim}$  were determined using high scan rates and found to be around 10 times lower than those obtained in acetonitrile.<sup>67</sup>

The trimerization of the 1,2-dimethoxybenzene (veratrole) was investigated in the same RTILs (Figure 4) and was found to follow a similar mechanism in ACN and in these RTILs.<sup>67</sup> The key intermediate is a dimer resulting from the oxidative coupling of dimethoxybenzene the production of which is rapidly followed by different electrochemical/chemical reactions, leading to the final trimer (Scheme 8). However, dimerization rate constants measured in RTILs were between 5 and 10 times smaller than those measured in acetonitrile, depending on the nature of RTILs.

Oxidative dimerization of *N,N*-dimethyl-*p*-toluidine is another example of electrochemical formation of a dimer,



**Scheme 9. Mechanism of Oxidative Dimerization of *N,N*-Dimethyl-*p*-toluidine According to Ref 165**


and the mechanism was investigated in detail in [Pyr<sub>4</sub>]-[NTf<sub>2</sub>].<sup>165</sup> The mechanism is different than those discussed previously since it involves the deprotonation of the radical cation of the *N,N*-dimethyl-*p*-toluidine by the starting molecule as a first and kinetic-determining step (Scheme 9).

Investigations of the kinetics using both cyclic voltammetry and chronoamperometry at microdisk electrodes have shown that the mechanism in the RTILs was consistent with that established in acetonitrile, involving dimerization of the *N,N*-dimethyl-*p*-toluidine following the proton transfer step. In this case, the kinetic rate constant for the deprotonation step in RTIL was found to be similar to the one measured in acetonitrile.<sup>165</sup>

**Cathodic Electrodimerization: Pinacolization.** Concerning the electrodimerization involving radical anion, the pinacolization of aromatic carbonyl compounds can be achieved from the electroreduction of the corresponding carbonyl compounds. This type of electroreduction was investigated both for synthesis applications and for fundamental studies.<sup>164,170,178</sup> The overall electrochemical process results in a competition between the pinacol and the alcohol formations. In the point of view of fundamental knowledge, this competition provides interesting information about the RTILs effects, since the distribution of the resulting products strongly depends on the nature of the electrolytic medium.

The reduction of benzaldehyde was investigated in [BMIm][NTf<sub>2</sub>] and [Pyr<sub>4</sub>][NTf<sub>2</sub>].<sup>164,178</sup> Two competitive processes occur after the first reduction of the benzaldehyde in the ionic liquids: the dimerization leading to the corresponding pinacol and the second reduction leading to the alcoholate. The apparent second-order rate constant,  $k_{\text{dim}}$ , for the dimerization was reported to be  $1.4 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ , and the pseudo-first-order rate constant,  $k_{\text{H}}$ , for the alcohol/stabilized alcoholate formation was in the 1000–1600  $\text{s}^{-1}$  range, which can be compared with the  $k_{\text{dim}} = 8.5 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $k_{\text{H}} = 8.5 \text{ s}^{-1}$  in DMF/TEAP and  $9.5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  in ACN/TEAP. These results suggest a different effect mainly based on acceleration of the protonation rate of the radical and little effect on the dimerization rate constant. However, it should be noticed that precise determination of the second-order rate constants may be somewhat imprecise because of the occurrence of two follow-up chemical reactions.

The electrodimerization of acetophenone was investigated in three ionic liquids ([BMIm][NTf<sub>2</sub>], [Me<sub>3</sub>BuN][NTf<sub>2</sub>], and [Et<sub>3</sub>BuN][NTf<sub>2</sub>]).<sup>170</sup> In contrast to the results obtained in molecular solvents, preparative scale electrochemical reduction showed the exclusive formation of the corresponding pinacol as a mixture of two diastereoisomers, *d,l* mixture and *meso* compound, and not of the corresponding alcohol. This change in the nature of the reactivity was explained by the existence of strong ion-pair associations between the charged radical anion and the cation of the RTILs. The dimerization rates between the two negatively charged radical acetophenone species, associated with the RTIL cations, increase considerably, by more than a factor of 10, and thus, dimerization becomes the predominant process (Table 4).

**Table 4. Electrochemical Data for Acetophenone in Ionic Liquids and in Conventional Electrolyte**

	$E^\circ$ (V) <sup>a</sup>	$k_{\text{dim}}$ (L mol <sup>-1</sup> s <sup>-1</sup> )
[BMIm][Tf <sub>2</sub> ]	−2.27	$\geq 4 \times 10^6$
[Et <sub>3</sub> BuN][NTf <sub>2</sub> ]	−2.60	$3\text{--}5 \times 10^5$
[Me <sub>3</sub> BuN][NTf <sub>2</sub> ]	−2.44	$1\text{--}2 \times 10^6$
Conventional electrolyte	−2.52 <sup>b</sup>	$2.7 \times 10^5$ <sup>c</sup>

<sup>a</sup> V vs ferrocene/ferrocenium redox couple. <sup>b</sup> In DMF with 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub>. <sup>c</sup> In EtOH with 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NOH.

The fastest dimerization rate was obtained in [BMIm][NTf<sub>2</sub>], indicating that associations are stronger in imidazolium-based RTILs than in the quaternary ammonium-based RTILs.

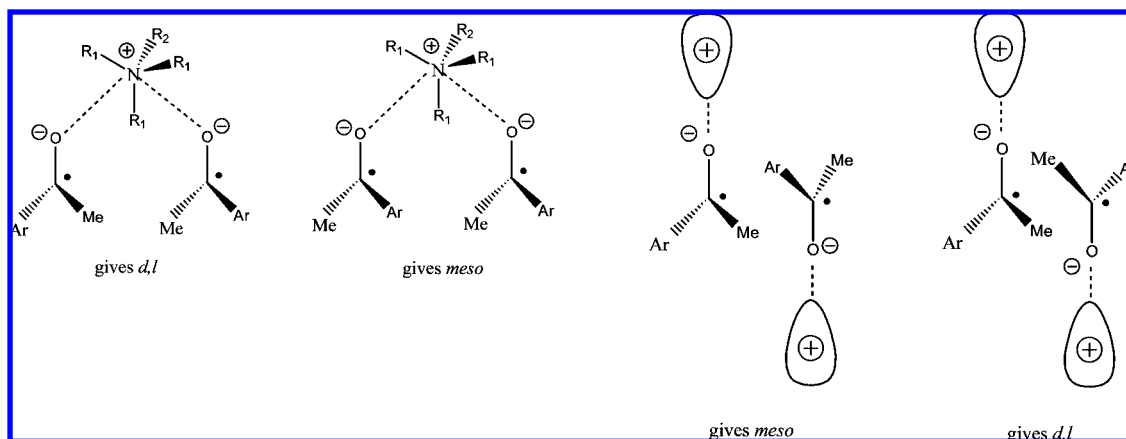
Simultaneously, variations in the stereoselectivity were observed depending on the nature of the cation of the RTIL. For the imidazolium-based ionic liquids, ion association between the radical anion and the cationic imidazolium promotes a head-to-tail configuration that decreases the stereoselectivity of the coupling reaction. In contrast, the ion associations with the ammonium cations were weaker and the anionic species are less efficiently stabilized, leading to a slower dimerization process than that in imidazolium-based RTILs. This weakness is postulated to maximize an “ion-bridging formation” (two or more cations with one radical anion) compared with “ion pairs” with one cation and one anion. The formation of the *d,l*-diastereoisomer is then favored because the cationic bridging exerts a strong sterically templating effect between two coupling anions (Figure 5).

Relative to the reactivity of aromatic ketone radical anion, the electrochemical reductions of a series of substituted benzophenones (benzophenone, 3-methylbenzophenone, 4,4'-dimethylbenzophenone, and 4,4'-dimethoxybenzophenone), investigated by cyclic voltammetry in [BMIm][NTf<sub>2</sub>], were found to be irreversible at low scan rates. Based on kinetics investigations, this irreversibility was ascribed to the protonation of the electrogenerated radical anion by the [BMIm] cation. Dimerization does not appear to be significant in this media.<sup>169</sup>

### 5.3. Bimolecular Reaction Rates in RTILs: Comparison between Electrochemical Investigations and Pulse Radiolysis Methods

Despite the fact that pulse radiolysis methods are not purely electrochemical, derived results can be easily compared with the data obtained from the electrochemical measurements. In pulse radiolysis, oxidizing or reducing species are produced by short pulse irradiation. The redox reactions produced the same species that one could obtain at an electrode, and consecutive reactivity can be monitored by UV–visible time-resolved spectroscopy. The first experiments were driven by the possibility of using RTILs in radiochemistry and concerned their stability upon  $\beta$  and  $\gamma$  irradiation.<sup>180</sup> Initially produced species depend on the considered ionic liquids, but these intermediates could easily be converted into the classical redox reactant similar to those produced in molecular solvents. Classical RTILs, such as those based on imidazolium salts or quaternary ammonium cation, proved to be ideal media for the generation of radical cations and anions by pulse radiolysis techniques.<sup>181,182</sup> Especially, solvated electron, which is a very strong reducing agent, was produced in [Me<sub>3</sub>BuN][NTf<sub>2</sub>] and in [BuP]-[NTf<sub>2</sub>].<sup>182–184</sup>





**Figure 5.** Steric interactions involved in the case of weak ion-pair formation between one ammonium cation and two radical anions and in the case of the formation of a strong ion pair between imidazolium cation and acetophenone radical anion. Reprinted with permission from ref 170. Copyright 2005 Royal Society of Chemistry.

Kinetic rate constants for the reaction of the solvated electron with several organic molecules have been measured. In  $[\text{Me}_3\text{BuN}][\text{NTf}_2]$ , reactions rates of the solvated electron with benzophenone, pyrene, or phenanthrene were found to be similar, in the range  $(1.3\text{--}1.7) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ .<sup>183</sup> Because these reactions are thermodynamically favored, they could be considered under diffusion control and thus offer a way to estimate the diffusion-limit rate constants in the RTILs. It is notable that only small variations are observed between the rate constants of the reactions of the solvated electron with different molecules. Considering that these reactions display different driving forces, this observation supports the hypothesis of diffusion control for these processes. These rates could be compared with estimations obtained for the diffusion-controlled limit for  $[\text{Me}_3\text{BuN}][\text{NTf}_2]$  and the equation  $k_{\text{diff}} = 8000RT/(3\eta)$  to  $1.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ .<sup>182</sup> This comparison indicates that the measured values exceed the estimated diffusion limit by an order of magnitude. Similar reaction kinetics was measured with the reaction of other radicals. Diffusion-controlled electron transfer kinetics was obtained between the pyridinyl and alkylpyridinyl radicals with duroquinone. As for the reduction with the solvated electron, experimental constants measured in different quaternary ammonium and pyridinium RTILs were higher than those predicted from the viscosity. It was found that the ratio between the measured diffusion limit and the estimated one is about 8 with  $[\text{MeBuN}]$  cation, 11 and 13 with the bigger  $[\text{Bu}_3\text{HexN}]$  and  $[\text{MeOct}_3\text{N}]$  cations, but only 5 with  $[\text{Pyr}_4]$  cation, which can be seen as a more compact and less flexible cation.<sup>184</sup> This effect was ascribed to the difference between the measured “macroviscosity” of the medium and the “microviscosity” in the immediate surroundings of the reactant.

Electron transfer kinetics was also studied for redox systems for which the reaction is under activation control using less reactive redox radicals. Kinetic constants measured in the RTILs were compared with the rates measured in molecular solvents ( $\text{H}_2\text{O}$  and alcohol). The oxidation of chlorpromazine or Trolox by  $\text{CCl}_3\text{O}_2^\bullet$  radicals was determined in different ionic liquids,  $[\text{BMIm}][\text{PF}_6]$ ,<sup>185</sup>  $[\text{BMIm}][\text{BF}_4]$ ,  $[\text{Pyr}_4][\text{BF}_4]$ , and  $[\text{MeBu}_3\text{N}][\text{NTf}_2]$ .<sup>182</sup> After correction from the effects of the diffusion limit, rate constants were found to be dependent on the ionic liquid, but their values were at least 2 orders of magnitude lower than those measured in water.<sup>182</sup> Other oxidants generated by pulse radiolysis were tested, for example,  $\text{Br}_2^{\bullet-}$ . The stability of

$\text{Br}_2^{\bullet-}$  was found to be much greater in the ionic liquid than in water. The oxidation rate of chlorpromazine by  $\text{Br}_2^{\bullet-}$  changes from  $6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  in water to  $1.1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  in  $[\text{MeBu}_3\text{N}][\text{NTf}_2]$ .<sup>186</sup> Kinetics of the reduction of duroquinone by benzophenone ketyl was measured in  $[\text{MeBu}_3\text{N}][\text{NTf}_2]$  and was also found to be much lower than that measured in water.<sup>186</sup> As other examples of electron transfer reduction, reactions of methyl viologen radical cation with quinones were found to be 3 or 4 orders of magnitude slower than those in  $[\text{Pyr}_4][\text{BF}_4]$ , water, or isopropanol.<sup>185</sup> As seen from these examples, rate constants generally decrease by at least 1 order of magnitude upon going from an aqueous solution to isopropanol and again by another order of magnitude upon going to the ionic liquid. It is rather difficult to rationalize these effects, and the part between activation and thermodynamic contributions remains unclear. For  $\text{Br}_2$ , it was suggested that the changes in the energy of solvation through their effects on the reduction potentials were the main factors affecting the electron transfer rate constants and thus the driving force of the reaction.<sup>186</sup>

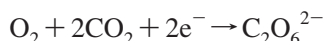
## 5.4. Electrochemical Reactivities of Inorganic Systems

### 5.4.1. Reduction of Oxygen

Reduction of oxygen has been extensively studied in aqueous and in organic solvents. In an aprotic molecular organic solvent,  $\text{O}_2$  is reversibly reduced to the superoxide  $\text{O}_2^{\bullet-}$ . Reduction of oxygen was investigated in some common ionic liquids. In quaternary ammonium or imidazolium-based ionic liquids,  $\text{O}_2^{\bullet-}$  was found to be chemically reversible.<sup>187</sup> As discussed above, one noticeable feature is the large difference between the diffusion coefficients of  $\text{O}_2$  and  $\text{O}_2^{\bullet-}$  (up to a factor 30). However, fitting of the data from cyclic voltammetry or chronoamperometry at microdisk electrodes demonstrated the stability of  $\text{O}_2^{\bullet-}$  in these media.<sup>74,75</sup> The same investigations were performed in quaternary phosphonium cations.<sup>187</sup> In this ionic liquid, the reduction of oxygen was found to be irreversible due to the phosphonium cation acting as a weak acid in a two-electron reduction process.

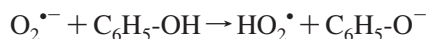
Working in imidazolium or quaternary ammonium RTILs allows investigations of the reactivity of  $\text{O}_2^{\bullet-}$  with other molecules. The reduction of  $\text{O}_2$  was studied in these media in presence of  $\text{CO}_2$ , which is reduced at a more negative potential.<sup>188</sup> A doubling of the current was observed and was

interpreted in terms of a ECE-DISP1 mechanism, in which  $O_2^{\bullet-}$  reacts with  $CO_2$  to finally produce  $C_2O_6^{2-}$ .

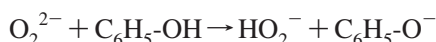


The reaction of  $CO_2$  with  $O_2$  was found to be the kinetic-determining step with a rate constant around  $1.4 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$  in  $[EMIm][NTf_2]$  and  $1.7 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$  in  $[Et_3BuN][NTf_2]$ , showing a similar reactivity of  $O_2^{\bullet-}$  in both ionic liquids.

Reactivity of  $O_2^{\bullet-}$  with phenol was investigated in  $[EMIm][NTf_2]$ .<sup>189</sup> However, in contrast to the behavior in organic solvent where  $O_2^{\bullet-}$  is known to be protonated by phenol, the cyclic voltammetry indicates that this reaction does not occur, or at least not to a large extent in this RTIL:



Only  $O_2^{2-}$ , which is a strong base, was able to deprotonate efficiently the phenol to produce the corresponding phenolate.



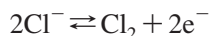
#### 5.4.2. Oxidation of Ammonia

Electrochemical oxidation of ammonia has been examined in several RTILs by Compton et al.<sup>190–192</sup> In the first investigations, voltammograms obtained in  $[EMIm][NTf_2]$  and in DMF have shown that similar responses are observed in each solvent with a broad oxidative wave and a new reductive process after the oxidation. It was deduced that the ammonium cation was formed after oxidation of ammonia, which is followed by deprotonation of ammonium to form ammonia and protons (Scheme 10).<sup>190</sup> Comparison of the response in several ionic liquids with different anions established the influence of the anion of the RTILs in the global oxidation mechanism.

Depending on the anion of the RTILs ( $A^-$ ), subtle changes in the mechanisms are observed.<sup>190</sup> In most cases, the protonated anion ( $AH$ ) of the RTIL is formed in a first step corresponding to the oxidation of  $NH_3$  to  $N_2$ , followed by the protonation of  $NH_3$  by the generated acid of the RTIL anion to form  $NH_4^+$ . In contrast, in  $[BMIm][PF_6]$ ,  $NH_4^+$  is formed prior to the formation of  $HPF_6$ .<sup>190</sup>

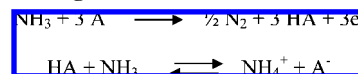
#### 5.4.3. Direct Oxidation of Halides and Metallic Halides in RTILs

The oxidations of halides,  $Cl^-$  and  $Br^-$ , display some different behaviors in RTILs than those observed in organic media. Oxidation of  $Cl^-$  in  $[BMIm][PF_6]$ , with large concentrations of  $[BMIm][Cl]$ , displays an irreversible process both on platinum and on graphite electrode. The main feature was that this oxidation does not lead to chlorine gas evolution but to the formation of oxidation products that stay in the RTILs in the form of complexes between  $Cl_2$  molecule and chloride ion where the  $Cl_3^-$  is the major product.<sup>129,193,194</sup>



Oxidation of  $Br^-$  was investigated in an imidazolium RTIL but with a different anion,  $[NTf_2]$ .<sup>195</sup> The proposed mechanism was the same as for  $Cl^-$ , involving first the direct oxidation of bromide,  $Br^-$ , to bromine,  $Br_2$ , followed by the homogeneous formation of tribromine anion,  $Br_3^-$ . However,

#### Scheme 10. Mechanism of Electrochemical Oxidation of Ammonia According to Ref 190



the equilibrium constant corresponding to the formation of  $Br_3^-$  was found to be 3 orders of magnitude smaller in the ionic liquid than in acetonitrile. However, direct comparison between results obtained with  $Cl^-$  and  $Br^-$  are difficult because the nature of the anion, which was different in each study, may influence this type of equilibrium.

A few works report on the behavior of metallic halides in RTILs. A part of this research was dedicated to the behavior of actinides in nonchloroaluminate RTILs. RTILs allow investigations on actinide chemistry without the unwanted side reactions existing in chloroaluminate ionic liquids.<sup>196</sup> For the first time, it was shown by a spectroscopic and voltammetric analysis in  $[BMIm][NTf_2]$  that some actinides(IV) ( $Np(IV)$  and  $Pu(IV)$ ) are able to form chloride complexes with a  $Cl^-/An(VI)$  ratio above 6/1.

The electrochemistry of gold was studied in detail in  $[BMIm][NTf_2]$  over different electrode materials:<sup>194</sup> gold, platinum, and glassy carbon. The reduction of  $AuCl_4^-$  salt forms in a first step  $AuCl_2^-$  before deposition as  $Au(0)$ .

#### 5.4.4. Redox Chemistry of Polyoxometalate Anions in Ionic Liquids

The impact of counteranions on the redox activity of POM anions is well-known to modify several aspects of the catalytic and aggregation behavior. The Keggin ion,  $\alpha-[PW_{12}O_{40}]^{3-}$  was investigated in  $[EMIm][PF_6]$  and  $[PMIm][PF_6]$  and compared with the behavior observed in acetonitrile.<sup>197</sup> Differential pulse voltammetry in these RTILs allows the observation of several electron transfers (up to 4). Reversible potentials were more positive in ACN than in the RTILs regardless of the electrolyte used in the molecular solvent. This was interpreted in terms of combined isomerization, ion-association, and redox processes and a greater degree of ion clustering in the RTILs because of the higher concentration of cation in the ionic liquid. It is notable that when associated with appropriate tetralkylphosphonium cations, Keggin ion  $\alpha-[PW_{12}O_{40}]^{3-}$  was found to provide an original family of ionic liquids, among them an ambient temperature “liquid POM”  $[Hex_4P][PW_{12}O_{40}]$ , which was somewhat highly viscous.<sup>198</sup> The electrochemical reduction of Mo and W polyoxometalate anions of isostructural pairs  $[\alpha-SiM_{12}O_{40}]^{4-}$  and  $[\alpha-S_2M_{18}O_{62}]^{4-}$  was investigated in  $[BMIm][PF_6]$  and up to six reversible one-electron transfer processes were detected.<sup>199</sup> Related electrochemical studies of the salt composed of the polyoxometalate anions with the cation of the RTILs  $[BMIm]_4[\alpha-SiM_{12}O_{40}]$  and  $[BMIm]_4[\alpha-S_2M_{18}O_{62}]^{4-}$  show that  $[BMIm]^+$  interacts with the surface of the anion in relation to the ability of the cation and polyoxometalate anions to form ion clusters in solution.

#### 5.5. Electrochemistry of Adhered Solid Phase of Redox Active Compounds in Ionic Liquids: Solid-State Voltammetry in Ionic Liquids

Solubility of compounds in some ionic liquids could sometimes be a problem for the achievement of cyclic voltammetry in RTILs. Bond et al. have developed a method based on so-called “solid-state voltammetry”, where micro-

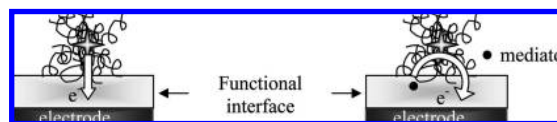
particles adhered onto a macroelectrode or a microelectrode are dipped in the ionic liquids.<sup>142</sup> The method was originally introduced to prepare reversible electrodes. The authors have observed the reversible potential obtained from voltammograms of solid particles of a series of solid ferrocene derivatives adhered to the electrode surface in [BMIm][PF<sub>6</sub>].<sup>145</sup> The conditions required to obtain apparent classic voltammetry in ionic liquids were investigated in detail and the different possible voltammetric patterns described. In RTILs, due to the slow dissolution kinetics and small diffusion coefficient, one can obtain voltammograms of the adhered solid particles that are often indistinguishable from the reversible voltammograms of species dissolved in the RTIL. Conditions to obtain an apparent equivalence with a diffusion-controlled process in which compounds are dissolved in the ionic liquid require a slow dissolution of the reactant and a fast rate for the dissolution of the product.<sup>142</sup>

The method was then extended to the case where a first-order follow-up chemical reaction occurs after the first electron transfer.<sup>200</sup> Electrochemical studies on ECE models in the case of *cis*–*trans* isomerization of organometallic compounds, *cis*-[Mn(CN)(CO)<sub>2</sub>(P(OPh)<sub>3</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>))] and *cis*-[W(CO)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)], have demonstrated the possibilities of the method and allow the measurements of the kinetic constants. The rate constants measured for the *cis*-Mn and *cis*-W in [BMIm][PF<sub>6</sub>], [EMIm][NTf<sub>2</sub>], [Pyr<sub>4</sub>][NTf<sub>2</sub>], and [Hex<sub>3</sub>C<sub>14</sub>H<sub>29</sub>P][(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>] were found to vary over the range 11–60 s<sup>−1</sup>, depending on the ionic liquid nature. Another extension of the method was proposed by the same authors. Microdroplets of a hydrophobic ionic liquid containing the microparticles were deposited on a working electrode, then investigated in an aqueous electrolyte solution.<sup>201</sup> Similar effects were found with the voltammetry of Fe(CN)<sub>6</sub><sup>3−</sup> deposited as microdroplets or thin films of an ionic liquid.<sup>202</sup> Several applications were reported concerning organometallic systems, oxidations of a series of highly insoluble decaphenylferrocene in [BMIm][PF<sub>6</sub>], [EMIm][NTf<sub>2</sub>], [Pyr<sub>4</sub>][NTf<sub>2</sub>], [Hex<sub>3</sub>(C<sub>14</sub>H<sub>29</sub>)P][(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>3</sub>],<sup>203</sup> and modular podand [1,3,5-tris(3-((ferrocenylmethyl)amino)pyridinium)-2,4,6-triethylbenzene][PF<sub>6</sub>].<sup>204</sup>

## 6. Bioelectrochemistry in the RTILs

The RTILs have been proven to be effective biocompatible media.<sup>205–207</sup> As an example, Rogers et al. reported the formation of thin films or beads from surface-functionalized cellulose using [BMIm][Cl], where a laccase enzyme was entrapped and exhibited a strong biocatalytic activity.<sup>207</sup> Bioelectrochemistry is an interdisciplinary field that combines biotechnology and electrochemistry. One of the challenging topics of this emerging field is the biointerfacial design of surfaces electrodes for both applications and fundamental purposes. Many research efforts have been then put in developing the direct electron transfer between redox biomolecules, mostly redox proteins or enzymes, and electrode surfaces.<sup>208</sup> The understanding of the mechanism of direct electron transfer from protein to electrode surface and the associated electrocatalytic reactions would allow modeling of the electron-transfer mechanism in biological systems and is potentially useful to tailor efficient biosensors or bioelectroanalytical devices. Direct electron transfer is often difficult to achieve because the redox core of proteins is deeply buried in the molecule. Redox reactions are more easily detected using mediator probes that act as reporter molecules between the protein and the electrode (Scheme 11). However, recent

**Scheme 11. Direct and Mediated Electron Transfer Processes between the Electrode Surface and a Biomolecule, Like a Protein**



advances in achieving direct electron transfer have been made by using modified electrodes where the proteins or the enzymes are confined.

Basically, two routes were explored in this specific area of electrochemistry: one is to use RTILs as components to modify electrode surfaces. The second one is to employ RTILs as electrolyte for directly investigating the electrochemical reactions.

### 6.1. RTILs as Components in Modified Electrodes

Many works reviewed in this section were inspired by the “microdroplets” method developed by Wadhawan et al.<sup>202</sup> and by Bond and Zhang (see section 5.5). Effectively adhering RTILs on electrode surfaces was found to be helpful to realize the direct electrochemistry of redox proteins. Even water-miscible RTILs including [BMIm][Cl], [BMIm][SCN], and [EtOHMIm][BF<sub>4</sub>] were reported to form molecular films on glassy carbon electrodes and to facilitate the direct electron transfer of HRP (horseradish peroxidase) in aqueous phosphate-buffered saline (PBS) solutions.<sup>209</sup> To increase their adherence onto the electrode, the RTILs were combined with different matrixes such as chitosan or Nafion.<sup>210–212</sup> Both Nafion and chitosan exhibit good biocompatibility. Mixing [BMIm][BF<sub>4</sub>] with chitosan or [BMIm][PF<sub>6</sub>] with Nafion membranes improved the conductivity of the membranes and yielded a suitable matrix for direct electrochemistry of HRP and hemoglobin (Hb). These composites films, where the proteins are entrapped, also provide a good microenvironment for HRP or Hb to retain their bioelectrocatalytic activity toward H<sub>2</sub>O<sub>2</sub>, oxygen, or trichloroacetic acid. Even more sophisticated composites were prepared by adding a sol–gel solution to form a sol/[EMIm][BF<sub>4</sub>]/Nafion/carbon electrode, whereby Hb could be tightly adsorbed on the surface.<sup>213</sup> Similar to carbon paste electrodes, the carbon ionic liquid electrode (CILE), where a RTIL is used as a binder in carbon paste electrode, offers an excellent platform for studying the direct electrochemistry and electrocatalytic activity of Hb or HRP.<sup>214,215</sup> Carbon nanotubes and carbon microbeads were incorporated into the water-immiscible [BMIm][PF<sub>6</sub>].<sup>216</sup> In particular, carbon nanotubes have been demonstrated to be physically cross-linked in the viscous RTILs, forming gels.<sup>217</sup> These carbon-composite materials mixed with HRP, Hb, or glucose oxidase were dropped onto gold or glassy carbon electrodes. The direct electrochemistry of heme proteins or glucose oxidase immobilized at these carbon materials has been investigated, and this promising biointerface promoted direct electron transfer and biocatalytic performance.<sup>216,218</sup> Closely related works using carbon nanotube composites, sometimes with gold nanoparticles, were also recently reported.<sup>219,220</sup>

A striking feature that can be pointed out in these works is that the reported redox potentials are roughly identical (around −0.34 V vs Ag/AgCl) for myoglobin, hemoglobin and HRP, whatever the method of immobilization chosen. Considering that HRP, Hb, and myoglobin possess a redox site of similar structure, this would suggest that, on the whole,



the protein or enzyme structure would not suffer from coating with RTILs. Indeed, in all these works, the integrity of the proteins was checked using UV–visible analyses to ensure the presence of the characteristic Soret absorption band.<sup>209–212,214,215</sup> For any of the RTIL-modified electrodes, no structural change of the protein or enzyme could be evidenced. However, note that the UV–vis analyses were performed using transparent quartz, glass-slide, or ITO substrates and not with the glassy carbon (or gold) electrodes used in the electrochemical measurements. Thus, in another recent work, de Groot et al. suggest that the strong affinity of the heme for adsorbing onto the carbon pyrolytic or graphite surface drives the heme release out of myoglobin native conformation.<sup>221</sup>

## 6.2. RTILs as Electrolytes

RTILs were used as supporting salts to analyze the redox signal of the biomolecules. Direct electrochemical response of myoglobin dissolved in an aqueous solution of 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate, [EtO-HMIm][BF<sub>4</sub>], was observed at a basal plane graphite electrode.<sup>222</sup> The work clearly demonstrated that the RTIL promoted the direct electron transfer between myoglobin and electrodes as compared with classical electrolytes. But further analyses suggested that the myoglobin was actually adsorbed on the electrode surface through entrapment or coating within the ionic liquids. Consequently, this closely resembles the microdroplets techniques described in section 5.5.

With neat RTILs as electrochemical solvents, a heme-model, the protoporphyrin IX iron(III) chloride, was investigated as free compound and compound linked to gold surfaces.<sup>223</sup> In both cases, the heme underwent a quasireversible one-electron reduction in [BMIm][PF<sub>6</sub>] and [Oct-MIm][PF<sub>6</sub>]. The redox potentials and heterogeneous electron-transfer rates were investigated for the free compound and were shown to vary as a function of the RTILs or added coordinating ligands. The heme-modified electrodes were shown to be fully operative in the RTILs. Fortified by these encouraging results, the authors expanded their study to cytochrome *c*, a heme-containing protein, adsorbed to gold electrodes. Unexpectedly, they found that cytochrome *c* did not retain its redox activity in both dried and wet ionic liquids, [BMIm][PF<sub>6</sub>] and [BMIm][NTf<sub>2</sub>], although a recovering of this activity could be achieved upon subsequent treatment with the aqueous buffer.<sup>224</sup> Detailed fluorescence and absorption spectroscopy studies were undertaken to rationalize the deleterious effect of the ionic liquids on the activity of cytochrome *c*.<sup>225</sup> The authors were able to determine that cationic and anionic components of the RTILs have distinct effects. The loss of redox activity caused by the imidazolium cations was due to a disruption of the self-assembled monolayer (SAM) where the protein is anchored. In contrast, the anion, and especially the [NTf<sub>2</sub>] anion drove a deep modification of the protein secondary structure (unfolding).<sup>225</sup> In partial contradiction with this work, voltammetry of different heme proteins and enzymes, Hb, myoglobin, HRP, and cytochrome *c*, entrapped in agarose hydrogel films could be readily performed in [BMIm][PF<sub>6</sub>].<sup>226</sup> Even after long time exposure to the anhydrous ionic liquids, the biomolecules display stable, well-defined redox systems. Moreover, the heme proteins entrapped in the agarose hydrogel catalyzed the electroreduction of trichloroacetic acid and *tert*-butyl hydroperoxide.<sup>226</sup> The inconsistency with the former work was postulated to be due

to a protective effect of the agarose hydrogel that contributed to the preservation of the native structure and redox property of the heme proteins.<sup>226</sup> A controversial *comment paper* re-examined the electrochemical results presented in this work<sup>226</sup> and proposed the occurrence of a strong modification of the proteins structure for interpreting the electrochemical responses.<sup>227</sup>

Despite some difficulties, the use of ionic liquids appears to be an interesting strategy for fabrication of nanostructured biointerfaces. The wide range of anions and cations available and the ease of fine-tuning the RTILs by appropriate combination or functionalization of anions and cations may open new paths in the construction of effective biocompatible biointerfaces. A recent paper reviewed some applications of ionic liquids in biosensors.<sup>228</sup>

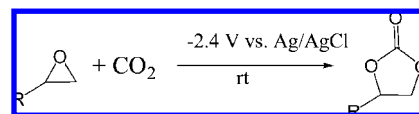
## 7. Organic Electrosynthesis

The RTILs are widely used as reaction media in many synthetic processes. Use of RTILs was primarily motivated to avoid employing volatile organic solvents, but many works state unexpected reactivity observed in these unconventional solvents, making RTILs invaluable reaction media.<sup>229</sup> In light of works reviewed in section 5, the RTILs that exhibit the highest conductivities can serve the same purpose for preparative-scale electrochemistry. In addition, their inherent conductivity suppresses the need for extraneous supporting salts, thus rendering the electrolysis technically easier and simplifying the product recovery. Surprisingly, use of RTILs in preparative-scale electrochemistry has been scarcely explored compared with organic synthesis.

### 7.1. Reduction of O<sub>2</sub> and CO<sub>2</sub>: Electroassisted Synthesis

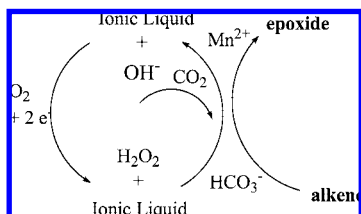
One of the first reports combining RTILs and electrosynthesis was a nonfaradic process in which a small amount of electricity was consumed to achieve the electrochemical activation of CO<sub>2</sub>.<sup>230</sup> Electrocatalytic species were thus generated to afford the addition of CO<sub>2</sub> to epoxides for the preparation of cyclic carbonates (Scheme 12). This process was found to be much simpler than those reported in conventional media.<sup>230</sup>

**Scheme 12. Electrochemical Preparation of Cyclic Carbonates**

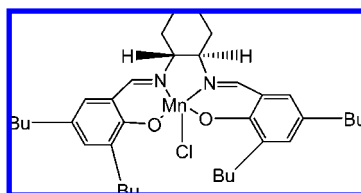


Hydrogen peroxide is an effective benign oxidant, but possible hazards related to the storage and transportation of concentrated H<sub>2</sub>O<sub>2</sub> contribute considerably to its cost. An electrochemical method was then proposed to generate and to activate H<sub>2</sub>O<sub>2</sub> *in situ*.<sup>231,232</sup> In the presence of NaOH, H<sub>2</sub>O<sub>2</sub> was electrogenerated in [BMIm][BF<sub>4</sub>] and used *in situ* for the epoxidation of electrophilic alkenes such as  $\alpha,\beta$ -unsaturated ketones.<sup>232</sup> Because this method requires strong alkaline conditions, it cannot be broadened to other classes of alkenes. Thus, the authors extended their work by adding carbon dioxide gas. This addition produced bicarbonate (HCO<sub>3</sub><sup>−</sup>) and the active peroxymonocarbonate (HCO<sub>4</sub><sup>−</sup>) species in the H<sub>2</sub>O<sub>2</sub>/RTIL/NaOH mixture, allowing neutralization of NaOH. Further addition of Mn<sup>2+</sup> as catalyst





**Figure 6.** Scheme of the electrochemical activation of hydrogen peroxide for epoxidation of alkenes.<sup>231</sup>



**Figure 7.** Structure of the Mn(III)-salen catalyst used for epoxidation of olefins.

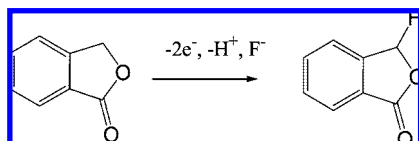
resulted in successful epoxidation of a wide range of alkenes (Figure 6).<sup>231</sup>

Note that the *in situ* electrochemical generation of  $\text{H}_2\text{O}_2$  was achieved from the reduction of oxygen to the superoxide  $\text{O}_2^{\bullet-}$  in the presence of water (or better in the presence of  $\text{OH}^-$ ). Using two protons from water,  $\text{O}_2^{\bullet-}$  species rapidly disproportionates into  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ .<sup>231,232</sup> As explained in preceding sections, use of ionic liquids makes it possible to electrogenerate stable superoxide ion. This facile generation of superoxide ion was also exploited for the preparation of functionalized siloxanes in good isolated yields by using pyridinium-based  $[\text{NTf}_2]$  salts.<sup>233</sup>

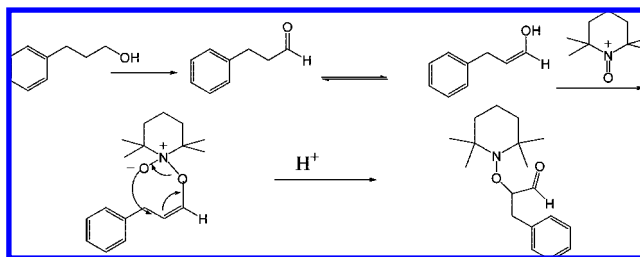
Mn(III)-salen catalyst (Figure 7) was tested in the activation of molecular oxygen for the epoxidation of olefins.<sup>234</sup> Cyclic voltammetry indicated the formation of a high-valence manganese-oxo active intermediate ( $\text{Mn(V)=O}^+$ ) in the ionic liquid in the presence of benzoic anhydride and 1-methylimidazole.<sup>234</sup> The rate of the epoxidation reaction was found to be fast enough to avoid the epoxidation being a competitive process with the formation of the oxo active intermediate.<sup>234</sup>

## 7.2. Selective Fluorination

Selective anodic fluorination was successfully carried out when RTILs were used as solvent/electrolytes.<sup>235</sup> The selective fluorination of organics is not straightforward due to the high reactivity of most electrophilic fluorinating agents. Focusing on phthalides, Fuchigami et al. demonstrated that high yields and selectivities were obtainable in  $[\text{EMIm}][\text{OTf}]$  containing quaternary ammonium polyfluorides ( $\text{Et}_3\text{N}\cdot 3\text{HF}$ ,  $\text{Et}_4\text{NF}\cdot 4\text{HF}$ ,  $\text{Et}_3\text{N}\cdot 5\text{HF}$ ) as fluorinating agents.<sup>236</sup>



**Figure 8.** Reversible oxidation of TEMPO.



**Figure 9.** Enolized aldehyde product reacting with the oxoammonium species during prolonged electrolysis.<sup>238</sup>

## 7.3. Oxidation of Alcohols

Electrochemical oxidations of alcohols to corresponding aldehydes or ketones were conducted in  $[\text{Pyr}_4][\text{NTf}_2]$ .<sup>237</sup> To operate a very clean and selective chemical transformation, the process was mediated by 5–12 mol % of a recyclable redox catalyst, TEMPO. Preliminary studies checked that TEMPO underwent reversible redox reaction to form the catalytically active oxoammonium species (Figure 8).

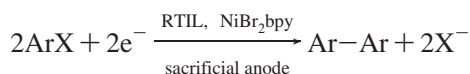
High viscosity of the RTIL that limited the mass transport of the catalyst was easily circumvented by addition of base and alcohol substrates, which significantly reduced the viscosity of the reaction media. Faradic efficiencies of 100% and 100% chemical selectivities were satisfactorily obtained, except for alcoholic substrates leading to enolizable carbonyl compounds. In this case, a prolonged electrolysis was found to lead to catalyst deactivation because of irreversible reaction between the active oxoammonium and the enolized product (Figure 9). To limit these undesired side-reactions, electrolyses must proceed to less than 1 F/mol. However, such behaviors were equally observed in conventional media.

## 7.4. Carbon–Carbon Bond Formation

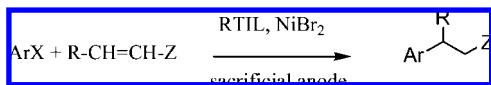
Direct electrooxidation of aromatic compounds, namely, mesitylene, anisole, naphthalene, and anthracene, in various ionic liquids allowed carbon–carbon bond formation and provided a simple method to isolate the corresponding dimers.<sup>239</sup>

Carbon–carbon bond formation can be also achieved from the electroreduction of organic halides. Direct dimerizations of alkyl and aryl halides were then tried in neat  $[\text{Oct-Im}][\text{BF}_4]$ . But the weak conductivity of this ionic liquid did not permit performance of an efficient electrosynthesis.<sup>240</sup> This drawback was easily overcome by the addition of a small amount of DMF (10% v/v). The electrolyses conducted in such conditions with a moderate cell voltage on a nickel cathode were able to produce the corresponding biaryl and bialkyl compounds. However, the isolated yields could be significantly improved by employing transition metal complexes as homogeneous catalysts. A nickel-catalyzed coupling reaction was then developed.<sup>240</sup> The Ni catalyst is electrochemically activated since the divalent  $\text{Ni}(\text{bpy})^{2+}$  complex is first reduced to the zero-valent  $\text{Ni}^0(\text{bpy})$  complex, which reacts by oxidative addition to the aromatic halide.

Poor activities were comparatively obtained in conventional solvents. Various ionic liquids were tested but  $[\text{EMIm}][\text{Otf}]$  was by far the most suitable ionic liquid, indicating a significant influence of the ionic components of the RTIL in the fluorination reaction.<sup>236</sup>



Excellent current efficiencies and good chemical yields were observed, with a nickel, a stainless steel, or an iron bar as sacrificial anodes. These results were as good as those observed in organic solvents.<sup>240</sup> With the same experimental conditions with NiBr<sub>2</sub> as catalyst, the work extended to the arylation of activated olefins.

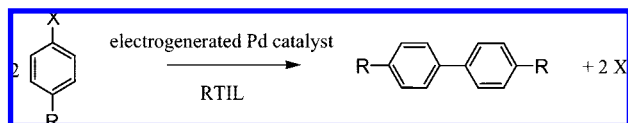


In conventional solvents, addition of nitrogenous cosolvent is necessary to complete this process. In the imidazolium-based ionic liquid, such an addition was useless. However, the yields and currents efficiencies, while good, were found to be lower than those obtained in conventional media.

Unlike this work, similar nickel electrocatalytic reductive dimerizations were successfully achieved in neat [BMIm]-[NTf<sub>2</sub>].<sup>241</sup> Without the need for adding extra solvent such as DMF, the authors reported the facile formation of biphenyl and 1,2-diphenylethane from the homocoupling of the parent aryl bromides. A major point of this work was the possibility of reusing the Ni catalyst (Ni(bpy)<sub>2</sub>) since the Ni(II) catalyst was found to remain totally in the ionic liquid after extraction of products.<sup>241</sup>

A more recent work reported on similar organic halide reductive couplings but using, this time, palladium nanoparticles as catalyst.<sup>242</sup>

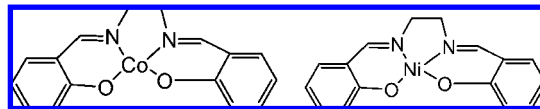
The main originality of the work came from the fact that



the palladium nanoparticles were generated *in situ* in the electrochemical cell containing a Pd anode and a Pt cathode. The anodic counter-reaction produced Pd<sup>2+</sup> ions from the Pd(0) anode. The Pd<sup>2+</sup> ions were reduced to adatoms at the Pt cathode and finally formed stabilized Pd(0) nanoparticles. The use of [OctMIm][BF<sub>4</sub>] as solvent allows the stabilization of the metal nanoparticles via an ion bilayer mechanism, without requiring any additional electrolytes or stabilizers. This kind of “ligand-free” catalysis is believed to be of main interest because it avoids using expensive ligands and allows catalyst recycling.<sup>242</sup> Careful kinetic analyses suggested that the catalytic cycle involved the formation of an ArX<sup>•-</sup> radical anion from a SET (single electron transfer) between a Pd cluster and the ArX molecules. The dissociation of the radical anion into Ar<sup>•</sup> and X<sup>-</sup> was followed by the coupling of the two aryl radicals. The oxidation of water to dioxygen and 2H<sup>+</sup> regenerated the Pd(0) clusters.<sup>242</sup>

## 7.5. Electrocatalyzed Dehalogenation Reactions

In relation with their possible electrocatalytic activities, electrochemistry of Co(II)– and Ni(II)–salen complexes have been investigated in [BMIm][PF<sub>6</sub>] and in [BMIm][BF<sub>4</sub>] (Figure 10).<sup>175,243</sup> As a general result, cyclic voltammetry or rotating disk electrode voltammetry of the complexes showed a similar behavior in the RTILs as those previously reported in various molecular solvents. For example, for the



**Figure 10.** Structures of the Co(II)– and Ni(II)–salen compounds.

well-known Co(II)–salen complex, well-defined and reversible redox waves were observed for the Co(II)/Co(III)–salen oxidation and Co(II)/Co(I)–salen reduction processes, with a positive-shifted potential for the Co(II)/Co(III) redox process as compared with those found in DMF or ACN.<sup>175</sup>

The potential of the electrocatalytic activity of the salen complexes was evaluated with dehalogenation processes as model reactions. Ni(II)–salen and Co(II)–salen were involved in the reductive dehalogenation reaction of iodoethane, Freon 113,<sup>243</sup> trichloroacetic acid, dichloroacetic acid, dibromoethane, and benzyl chloride.<sup>175</sup> With mechanisms almost unchanged compared with those in conventional solvents, the electrogenerated Ni(I)– or Co(I)–salen complexes showed a strong electrocatalytic activity for the carbon–halogen bond cleavage.<sup>175,243</sup> As an example, a 600 mV positive shift of the reduction potential together with a strong increase of the cathodic current is observed in [BMIm][BF<sub>4</sub>] for the reduction of iodoethane.<sup>243</sup>

In a very recent work, dehalogenation reactions of Freon derivatives were also successfully achieved without employing a homogeneous catalyst.<sup>176,244</sup> Owing to the use of a Ag cathode that exhibited electrocatalytic activity, direct reductive electrochemical activation of freons were observed in several RTILs.<sup>176</sup> While no difference between RTILs and conventional solvents was evidenced for this process, the nonvolatile character of the RTILs would be highly beneficial. Since the cathodic products of the reactions are volatile gases, product recovery should be a trivial process in the RTILs.<sup>176</sup>

Vitamin B12 (cyanocobalamin) and derivatives are considered as among the most effective catalysts for dehalogenation reactions. The electrochemistry of vitamin B12 was investigated in water/[BMIm][OTf] mixture (5/95% v/v) since the cyanocobalamin could not be dissolved in dry ionic liquid.<sup>245</sup> Interestingly, the use of ionic liquids allowed the observation of competing oxidation–reduction processes that are difficult to detect in conventional solvents. Reduction of vicinal dibromoalkanes<sup>245</sup> or DDT<sup>246</sup> was performed in the presence of vitamin B12 or hydrophobic derivatives in [BMIm][OTf]/water mixtures and in [BMIm][BF<sub>4</sub>], respectively.<sup>245,246</sup> Both works mentioned the high efficiency of the electrocatalytic effect due to vitamin B12<sup>245,246</sup> and even an enhanced reactivity in [BMIm][BF<sub>4</sub>] as compared with DMF medium.<sup>246</sup> But Compton et al. observed a somewhat unexpected smaller magnitude of the electrocatalyzed reduction wave compared with the uncatalyzed one.<sup>245</sup> This phenomenon was rationalized by considering the heterogeneous nature of water/RTILs mixture. The rate of the determining step reaction, which is the bimolecular reaction between the electrogenerated Co(I) form of the vitamin B12 with the dibromide compounds, was thought to be affected by reactants partitioning between the phases.<sup>202</sup> In contrast, a regular increased wave amplitude was reported for the electrocatalyzed reduction of DDT.<sup>246</sup>

## 7.6. Sono(electro)chemistry in RTILs

Many of works reviewed in this section outlined the slow mass transfer of reactants, due to the high viscosity of the

RTILs, as a main drawback for developing large-scale electrosyntheses in the RTILs. On the whole, the authors recommended to add small amounts of organic solvents or to heat up the reaction media to 40–50 °C. A different elegant method was proposed by Compton et al.<sup>247</sup> Combining sonochemistry and electrochemistry, *N*-methylphthalimide was selectively reduced to 3-hydroxy-2-methylisindolin-1-one in the presence of phenol. Owing to ultrasound, higher conversions and charge efficiency were observed.<sup>247</sup> Unfortunately, some decomposition of the ionic liquids was suspected to occur under exposure to ultrasound.<sup>248</sup>

## 8. Conducting Polymers

Over the past two decades, conducting polymers produced upon electrooxidative polymerization of appropriate monomers have attracted attention due to their interesting electrical and optical properties. These properties have led the conducting polymers to be incorporated in chemical sensors, batteries, supercapacitors, conducting textiles, electrochromic devices, and light-emitting diodes, to mention a few. For all these applications, the use of conventional electrolytes (volatile molecular solvent and supporting salts) may represent a limitation because of evaporation of solvent or aging and degradation of the electrolytes.<sup>249</sup> The nonvolatility and high thermal stability of the ionic liquids rapidly made them very attractive electrolytes for this field of electrochemistry.<sup>250</sup> Moreover, since the electrolyte used for the preparation of the conducting polymers has also a key influence on the properties of the resulting materials, including conductivity, electrochemical stability and efficiency, and mechanical properties, the RTILs have also attracted growing interest as media to perform the electrosynthesis of these polymers.

### 8.1. Preparation of Conducting Polymers in RTILs

The potential of the RTILs as media for electrosynthesis of conducting polymers was first demonstrated in the late 1980s for polyfluorene,<sup>251,252</sup> polythiophene,<sup>253</sup> or polyphenylene<sup>254</sup> in chloroaluminate ionic liquids. But the high sensitivity of these ionic liquids toward water produced HCl that led to rapid decomposition of the polymer. In this respect, nonchloroaluminate ionic liquids, which are under investigation in this review, have proven to be superior media. Several electrochemical polymerization reactions have been conducted in RTILs and showed promising results. One should remember that electrooxidative polymerization involves the coupling between two radical cations of the monomer or of the produced oligomers.<sup>177</sup> It is likely that stabilizing interactions should play a favorable role in the coupling between two charged species, explaining the good results noticed in RTILs.

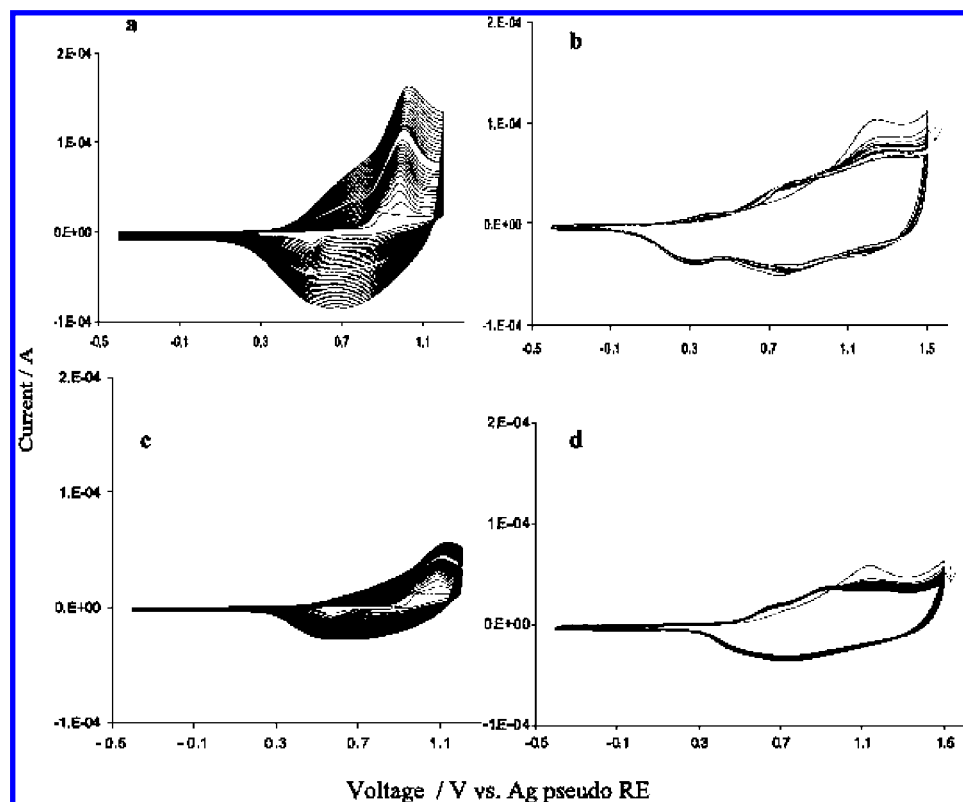
Electrosynthesis of polypyrrole (PPy) in [BMIm][PF<sub>6</sub>] on iron and Pt<sup>255,256</sup> and in [EMIm][OTf], [EMIm][BF<sub>4</sub>], and [EMIm][PF<sub>6</sub>] on Pt,<sup>257</sup> of poly(3,4-ethylenedioxythiophene) (PEDOT) in [EMIm][NTf<sub>2</sub>], [Pyr<sub>4</sub>][NTf<sub>2</sub>], [BMIm][PF<sub>6</sub>], and [BMIm][BF<sub>4</sub>] on Pt<sup>258,259</sup> or in [EMIm][BETI] on “K-glass”,<sup>260</sup> of poly(3-(4-fluorophenyl)thiophene) in [EMIm][NTf<sub>2</sub>] and [EEMIm][NTf<sub>2</sub>] on Pt,<sup>261</sup> of poly(*para*-phenylene) (PPP) in 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate on Pt,<sup>262</sup> of poly(3-chlorothiophene) in [BMIm][PF<sub>6</sub>] on Pt,<sup>263</sup> and of polythiophene in [EMIm][NTf<sub>2</sub>] or [Pyr<sub>4</sub>][NTf<sub>2</sub>] on Pt<sup>264</sup> have been studied.

All these works resulted in the formation of electroactive and stable polymer films that resembled those obtained in conventional media. For instance, FTIR spectroscopy of PEDOT films electrosynthesized in [BMIm][PF<sub>6</sub>] or in [BMIm][BF<sub>4</sub>] showed the same characteristic spectra as those reported for PEDOT films prepared in common organic media.<sup>259</sup> UV–visible analyses showed that the average conjugation length was roughly the same for both media.<sup>259</sup>

Easier or more efficient preparation of conducting polymers films in neat ionic liquids as compared with conventional media was highlighted in some works.<sup>257,258,262,263</sup> The electropolymerization of benzene could be achieved with milder conditions in RTILs than in the usually employed concentrated sulfuric acid or liquid SO<sub>2</sub>.<sup>262</sup> As mentioned by the authors, the use of ionic liquids would enable further studies on the nanoscale with *in situ* scanning tunneling microscopy that would be totally precluded in aggressive media like 18 M sulfuric acid or liquid SO<sub>2</sub>.<sup>262</sup> Comparison of electropolymerization of pyrrole in neat [EMIm][OTf], as well as in [EMIm][OTf] diluted in CH<sub>3</sub>CN or H<sub>2</sub>O (0.1 mol L<sup>-1</sup>), demonstrated that the electropolymerization is more efficient in the neat ionic liquid.<sup>257</sup> This result strengthens the idea that ionic liquids are powerful media for the electrochemical generation of conducting polymers films. However, there is a practical point that is worth outlining. While typical 10<sup>-2</sup> to 10<sup>-1</sup> mol L<sup>-1</sup> monomer concentrations have been used in conventional organic solvents to produce conducting polymers films,<sup>249</sup> higher concentrations (10<sup>-1</sup> to 5 × 10<sup>-1</sup> mol L<sup>-1</sup>) are generally used in the RTILs.<sup>255–259,261–265</sup> This may represent a major drawback when working with noncommercially available monomers.

The influence of the nature of the RTILs toward the preparation, the morphology, and the electrochemical activity of polymers has been investigated.<sup>257,258,264</sup> The electropolymerization of pyrrole was found to be more efficient in [EMIm][OTf] than in [EMIm][BF<sub>4</sub>] and [EMIm][PF<sub>6</sub>], with a formation of smoother and more highly doped polymer films than those from the latter RTILs. This result indicates a significant influence of the anion.<sup>257</sup> Although the influence of the nature of the anion in the electropolymerization process is expected since anions are generally acknowledged as a source of dopants that are required when the polymer is oxidized, the authors attribute the increased growth of the PPy to the higher viscosity of the triflate RTIL.<sup>257</sup> Thiophene, bithiophene, and terthiophene have been polymerized in imidazolium- and pyrrolidinium-based [NTf<sub>2</sub>] ionic liquids (Figure 11). Whatever the monomer, use of the pyrrolidinium salts led to polythiophene films that were smoother and denser and had a lower electroactive surface than those from the imidazolium salts.<sup>264</sup>

Similar studies performed on PEDOT materials also indicated a strong influence of the cations. The PEDOT film growth was faster in [EMIm][NTf<sub>2</sub>] than in acetonitrile/tetrabutylammonium perchlorate<sup>258,266</sup> but slower in [Pyr<sub>4</sub>][NTf<sub>2</sub>].<sup>258</sup> These differences were primarily attributed to differences in solvent viscosity and conductivity. Parallel differences were also observed in the electrochemical activities of the films, demonstrating that cations played an effective role in the charging process of the PEDOT films. As a general result, the nature of both anion and cation strongly influence the doping processes in the conducting polymers, directing the morphology and the properties of the conducting polymers films.



**Figure 11.** Cyclic voltammograms of terthiophene polymerization (left) in [EMIm][NTf<sub>2</sub>] (top) and in [Pyr<sub>4</sub>][NTf<sub>2</sub>] (bottom) and electrochemical activity of the corresponding grown polymers (right) in [EMIm][NTf<sub>2</sub>] (top) and in [Pyr<sub>4</sub>][NTf<sub>2</sub>] (bottom). Reprinted with permission from ref 264. Copyright 2005 Elsevier.

Some additional works offer, in our opinion, original synthesis concepts. The RTILs can be advantageously used to achieve the electrochemical functionalization of single-walled carbon nanotubes (SWNTs) with polyaniline (PANi).<sup>215</sup> Because SWNTs can be well separated in the RTILs and form a significantly untangled network, a large amount of each SWNT is able to be functionalized by PANi films in [BMIm][PF<sub>6</sub>] containing trifluoroacetic acid. The structural characterization showed that PANi has been covalently bound to the SWNTs. This demonstrates that SWNTs were hardly incorporated as big dopants in the polymer matrix.<sup>215</sup> The morphology of the materials was examined with SEM. PANi was seen to wrap around the SWNT dispersed onto the electrode surface and coated the whole surface when the polymerization was complete. The electrode substrate was modified with aniline silane, and the SWNTs dispersed in RTILs at the vicinity of the electrode acted as a 3D working electrode. During the course of the electropolymerization, the SWNTs were believed to function as a collection of small working electrodes where the electropolymerization of aniline occurred.<sup>215</sup>

Pyrrole was electropolymerized in RTILs using a platinum wire that was vertically placed into the cell, completely immersed in the RTILs and touching the bottom of the cell. It was observed that if the polymerization started as an initial layer on a section of the working electrode, prolonged electrosynthesis led to a growth of the polymer film along the surface of the ionic liquid. This solution–surface electropolymerization was found to occur with a large range of RTILs.<sup>267</sup>

Fibrils of polypyrrole, polythiophene, and PEDOT were obtained from closely related interfacial polymerization. Using this time a *chemical* polymerization route, a biphasic

ionic liquid/water system with the oxidant dissolved in the aqueous phase and the monomers dissolved in the RTILs, allows the polymerization to occur at this RTIL/water interface. The resulting polymers consisted of fibrils about 50 nm wide and several hundreds of nanometers long.<sup>268</sup>

## 8.2. Properties of Conducting Polymers in RTILs

Fundamental work has been undertaken to gain further insights in the doping/undoping processes. It is worth emphasizing that the doping (or charging) process is of major concern for both the production of the polymers and their electrochemical activities. Whatever the electrochemical method chosen for performing the electropolymerization, polymers are produced in their oxidized form and insertion of anions (doping process) is necessary to counterbalance the positive charges.<sup>249</sup> If cyclic voltammetry is used, successive oxidation/reduction scans are operated with the as-produced polymers switching between oxidized and neutral states. Obviously, this requires successive insertion and expulsion of anions.<sup>249</sup> An absolutely equivalent mechanism of anionic insertion/expulsion is found for the electrochemical activity of a deposited polymer film. The redox charging process of PEDOT films in [EMIm][NTf<sub>2</sub>] was carefully studied by potential step experiments and electrochemical impedance spectroscopy.<sup>258,266,269</sup> The PEDOT films grown in acetonitrile medium displayed a capacitive behavior, but instead of displaying the classical anion insertion/expulsion mechanism during the oxidation, the PEDOT films exchanged imidazolium cations (expulsion), while anions were trapped in the polymer film and could be considered as immobile species.<sup>266,269,270</sup> The electrochemical behavior of the PEDOT films formed in



acetonitrile then cycled in [EMIm][NTf<sub>2</sub>] was however different from that of PEDOT films formed and cycled in [EMIm][NTf<sub>2</sub>].<sup>258,266,269,270</sup> Indeed, the former exhibited two anodic and two cathodic peaks. Randriamahazaka et al. attributed these patterns to the coexistence of two different zones: a compact layer consisting of highly conjugated and rigid chains whose oxidation was located to the lowest potentials and a more open zone with oxidation potential at a more positive value.<sup>269,270</sup> Note that PEDOT films electrochemically synthesized in [EMIm][NTf<sub>2</sub>] exhibited only one anodic and one cathodic peak.<sup>266</sup> Nevertheless, the cationic exchange observed with PEDOT formed in acetonitrile was found to be also valid for PEDOT films produced in RTILs.<sup>261,266,271–273</sup> An electrochemical quartz-crystal microbalance (EQCM) study of poly-*para*-phenylene film in 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate demonstrated that redox cycling is accompanied by anion and cation exchanges. With increasing scan rate, cation exchange became prevalent over anion exchange, indicating a faster kinetics for the cation expulsion.<sup>271</sup> PEDOT films synthesized and cycled in RTILs containing bulky anions showed anionic potentiometric responses in aqueous KCl, indicating that the anions were still mobile in the polymer and tended to exchange with Cl<sup>−</sup> ions from the solution.<sup>272</sup> In contrast, only cationic exchanges were observed in the ionic liquids.<sup>272</sup> As an assessment, these basic studies evidence the importance of the choice of the cation and conclude that the oxidation kinetics (expulsion of cations) is facilitated over that of reduction (insertion of cation) in the RTILs.

Several works reported improved properties that were exhibited by the polymers when prepared in the RTILs or when prepared in conventional electrolytes then cycled in RTILs such as an increase of the conductivity,<sup>256,257</sup> a better electrochemical capacity,<sup>257</sup> or an enhanced cycling stability.<sup>265,273–275</sup> These results boost the use of RTILs as electrolyte in electrochemical devices involving conducting polymers.<sup>250,274–276</sup> As examples, while operating electrochromic alphanumeric displays based on PANi and PEDOT were described using [BMIm][BF<sub>4</sub>],<sup>274</sup> the use of RTILs in mechanical actuators were found to improve actuator performance in terms of cycle life and strain under load.<sup>273</sup> In contrast, a clear decrease of the electroactivity upon repetitive cycling was reported by Bélanger et al. concerning poly(3-(4-fluorophenyl)thiophene) films because of gradual deswelling of the polymer in the RTILs.<sup>261</sup>

## 9. Conclusion

Most of the common electrochemical methods have been used with success for electrochemical detailed investigations concerning all the physical and chemical aspects of RTILs. Besides the classical cyclic voltammetry on millimetric electrodes, most sophisticated techniques have been proven to be suitable in RTILs. These methods, including fast microsecond time scale transient electrochemistry, steady-state voltammetry at microdisk electrodes, and scanning electrochemical microscopy, open a way for investigating a number of processes. However, several precautions have to be taken by the electrochemist to ascertain the validity of the experiments due to the slowness of the diffusion processes in RTILs. By taking into account these particular aspects of the electrochemistry in RTILs, detailed investigations of the reactivity of organic compounds are possible in RTILs. The analysis of their electrochemical response based

on the competition between the diffusion rate and the chemical reaction kinetics provide accurate data to account for reactivity.

From the examples presented in this review, we can conclude that the main reactivity patterns involving electro-generated species in RTILs are for the most part maintained when a reaction passes from a conventional solvent to a RTIL. Most of the electrochemical reactions were successfully conducted in the RTILs. However, specific interactions with the cation of the RTILs in the case of radical anion or with the anion of the RTILs in the case of the radical cation can play a major role and lead to subtle modifications. Especially, reaction kinetics or product distributions may be highly sensitive to the nature of the ions that compose the RTILs.

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