

Electrochemistry of 1-Butyl-3-methyl-1*H*-imidazolium Tetrafluoroborate Ionic Liquid

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The electrochemistry of 1-butyl-3-methyl-1*H*-imidazolium tetrafluoroborate (BmimBF₄) ionic liquid was investigated by cyclic voltammetry and Osteryoung square wave voltammetry. Impurity chloride was identified, its concentration was determined and a way to eliminate it was demonstrated. Constant current electrolysis of BmimBF₄ was performed and products were analyzed by ¹H, ¹³C, and ¹⁹F-NMR and gas chromatography-mass spectrometry. BF₃ and fluorocarbons are produced at the anode while Bmim⁺ undergoes dimerization and dealkylation reactions at the cathode after reduction to a carbene. © 2003 The Electrochemical Society. [DOI: 10.1149/1.1568740] All rights reserved.

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As more and more applications of air stable room temperature ionic liquids such as 1-ethyl-3-methyl-1H-imidazolium tetrafluo-1-butyl-3-methyl-1*H*-imidazolium roborate. tetrafluoroborate (BmimBF₄), and hexafluorophosphate (PF_6^-) are explored, it is important to know the nature and amount of impurities in the ionic liquids. Tetrafluoroborates can be prepared by reacting imidazolium chloride salts with $NaBF_4$, ¹ NH_4BF_4 , ² $AgBF_4$, ³ HBF_4 , ⁴ or HF + BF_3 ;⁵ hexafluorophosphates can be prepared through KPF₆ or HPF_6 .⁶ Among the reactants, $NaBF_4$, NH_4BF_4 , and $AgBF_4$ produce a salt, i.e., NaCl, NH₄Cl, and AgCl, respectively, which has a limited solubility in the ionic liquid, leaving some chloride impurity behind. This has become a concern in some ionic liquid applications, especially in catalysis reactions because impurity chloride has complexing ability.⁷ The HBF₄ method produces HCl as a byproduct, which is volatile and easy to remove; this method is expected to produce a high purity product and is easy to carry out. The HF + BF₃ method involves all volatile compounds which are also easily removed, but they are dangerous and toxic. Chloride concentrations have been determined by potentiometry,⁸ gravimetry,⁹ titrimetry (Volhard's method),¹⁰ cathodic stripping voltammetry,¹¹ or with an ion selective electrode.¹² As both chloride and tetrafluoroborate precipitate with silver and mercuric ions, tetrafluoroborate will interfere in some of the methods mentioned above. In this paper, an electrochemical method is described for the determination of the chloride concentration in BmimBF₄ ionic liquid. Constant potential electrolysis was used to oxidize residual chloride to eliminate it from the ionic liquid. When this ionic liquid is electrolyzed, reduction of imidazolium cation takes place at the cathodic limit,¹³ but the details of the reduction have tended to be neglected. Moreover the oxidation reaction at the anodic limit has not been explored.¹⁴ It is the further intention of this paper to shed some light on the cathodic and anodic reactions at the electrochemical limits using platinum electrodes. Constant current electrolysis was utilized to investigate the reactions, and products were analyzed by NMR and gas chromatography-mass spectrometry (GC-MS).

Experimental

Semiconductor grade HCl was supplied by Matheson gas products, Inc. BmimBF₄ was synthesized by reacting equal moles of BmimCl with NaBF₄ in acetone,¹ stirring at room temperature for 24 h, filtering and vacuum drying overnight at 50°C; a yield of over 90% was obtained routinely.

Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) experiments were performed on a BAS 100 W station system. The three electrodes were a Pt counter electrode and working electrode, and a Ag wire immersed in $AgBF_4$ saturated

BmimBF₄ ionic liquid (AgBF₄ solubility in BmimBF₄ is *ca*. 0.2 M) as the reference electrode; the latter was immersed in the same ionic liquid separated from the cell electrolyte by a 5 μ m porosity frit. The working electrode was polished with 1 μ m diamond (Bioanalytical Systems). The frit was soaked in the electrolyte prior to electrochemical studies. Bulk electrolysis (BE) was performed at a potential of 2 V until the current ratio reached 1%. A comparison cyclic voltammogram was obtained after the electrolysis. Constant current electrolysis was performed with a Sargent coulometric current source model IV and a 3466A Hewlett Packard digital multimeter. Electrolysis was conducted at 9.2 mA for 12 h with large platinum electrodes (3 × 4 cm) in 20 g of BmimBF₄, and the two compartments were separated by a fine frit and stirred throughout.

GC-MS analysis.—Samples were analyzed by a HP 5890 capillary gas chromatograph coupled with a Finnigan Incos 50 mass spectrometer-quadrupole analyzer, which has a mass range of 0-1000 amu, electronic ionization (EI) 70 eV, and a vacuum system reaching 10^{-5} Torr. For the GC part, a 15 m DB1 fused silica capillary with i.d. = 0.25 mm, thickness = 0.25 μ m was used.¹⁵

¹*H*, ¹³*C*, and ¹⁹*F*-nuclear magnetic resonance (*NMR*).—NMR spectra were obtained with a Bruker AC 200 MHz NMR spectrometer. DMSO-d₆ was sealed into a capillary and used as the external standard. ¹⁹*F*-NMR was calibrated with CF₃COOH.

Results and Discussion

Cyclic voltammetry of BmimBF₄ and the identification of chloride.—BmimBF₄ with Pt electrodes yielded an electrochemical window of 4.9 V (+2.9 to -2.0 V vs. Ag/AgBF₄) (Fig. 1), wider than that of EmimBF₄ (4.5 V, +2.5 to -2.0 V vs. Ag/AgCl).² Sweeping positively from 0 V there was no oxidation peak until 2000 mV (peak II), and the anodic limit was at +2.9 V. Sweeping negatively from 0 V, there was no reduction peak until -2 V but after reversal at -2 V, there appeared an oxidation peak at -0.13 V (peak I) which was dependent on the previous reduction potential. Both the oxidation potential and oxidation current for peak I are directly related to the previous reduction potential. When the cathodic end potential moved from -2 to -1.5 V, peak I was reduced in size from 150 to 8 $\mu A,$ and the peak potential shifted from +0.2to -0.13 V. From the above observation, it is concluded that peak I is due to the oxidation of the reduction product at the low potential limit, i.e., the oxidation of the reduction product of 1-butyl-3methyl-1H-imidazolium cation, which is in accordance with previous reports.4,13 However, the electrochemical window reported by Katayama et al.⁴ was only 4.3 V, from +1.3 to -3.0 V, their oxidation potential limit probably being peak II in Fig. 1. The oxidation potentials for the reduction product of imidazolium⁴ appeared at -1.5 and -0.9 V; this may be attributed to the different cation: 1-ethyl-3-methyl-1H-imidazolium vs. 1-butyl-3-methyl-1H-imidazolium.

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Figure 1. Cyclic voltammograms of $BmimBF_4$ on 1 mm Pt electrode at room temperature, scan rate: 100 mV/s.

The oxidation peak at *ca.* 2 V (peak II) is due to the chloride impurity in the ionic liquid, which is confirmed by the dissolution of either 1-butyl-3-methyl-1*H*-imidazolium chloride or HCl gas in the ionic liquid. OSWV indicated that the magnitude of peak II increases with increasing BmimCl added. Change in initial potential and potential limits had no effect on peak II, but adding HCl to BmimBF₄ also showed an increased current at peak II in the OSWV voltammogram (Fig. 2), confirming that peak II was related to chloride. OSWV profiles of BmimBF₄ showed two small peaks at +2 and +2.3 V with current density of 0.1 mA/cm². After bubbling HCl through, both peaks increased, especially the peak at +2 V (Fig. 2). Adding HCl to the ionic liquid resulted in a narrowed electrochemical window at the reduction limit presumably due to the electrode reaction of HCl₂⁻.¹⁶

Sweeping negatively from 0 mV, there was no peak at -0.9 V, but upon reversal at the second cycle there was a reduction peak at -0.9 V (peak III). This showed that peak III was related to the oxidation limit, but did not originate from the original ionic liquid. The higher the oxidation potential, the larger the reduction current of peak III. Hence it was the reduction of either the oxidation product of BF₄- or the Pt electrode.

Determination of chloride concentration and its removal from $BmimBF_4$.—After the chloride peak was identified, the standard addition method with OSWV was applied to the determination of the chloride concentration: in 1.5 mL BmimBF₄, the current for impurity is 4.9 µA, adding 20 mg of BmimCl increased the current to 56 μ A, the current reached 267 μ A when 96 mg of BmimCl was added, a linear relationship between current and five additions of BmimCl added was obtained at 2.8 mM was obtained for the chloride concentration in the ionic liquid prepared by metathesis using NaBF4. The reproducibility of the data was satisfactory, with a standard deviation of 0.54 µA relative to 10.5 µA. Compared to Seddon's method of determining the concentration of chloride (Volhard wet chemical method and chloride selective electrode method), the detection limit of OSWV method is much lower. They reported 516 or 12 mM¹⁷ (if using chilled water-extraction preparation) of chloride in BmimBF₄ ionic liquid.

Constant potential electrolysis was applied to oxidize chloride to make the ionic liquid free of this complexing ligand. CVs and OS-



Figure 2. OSWV profiles of $BmimBF_4$ (1) blank, (2) with HCl and (3) with more HCl, square wave amplitude 25 mV, step voltage 4 mV, frequency 15 Hz.

WVs before and after the electrolysis indicated that this was an effective way of reducing Cl^- , to a level lower than the detection limit of OSWV.

Constant current electrolysis of $BmimBF_4$.—During the electrolysis of *ca.* 20 g of $BmimBF_4$ some gas bubbles appeared at the cathode, then gradually two layers formed, the upper one clear and red, the lower one opaque and red. The anode compartment changed color to dark brown; no gas bubbles were noticed on the anode, but after some time white fumes were observed in the homogeneous ionic liquid. These fumes could be removed by evacuation and 1.4 g of product was collected in a liquid nitrogen trap containing diethyl ether. The weights of Pt electrodes were unchanged within 0.1 mg.

The products after electrolysis were separated as anodic electrolyte, lower and upper layer cathodic electrolyte, and ether condensate from the anode compartment. They were analyzed by ¹H, ¹³C, and ¹⁹F-NMR and GC-MS.

 19 F-NMR showed two peaks for BmimBF₄ at -145.96 and -146.01 ppm, one large, one small without fine structure. Theoreti-

Table I.	¹⁹ F-NMR	data for	electrolysis	of BmimBF ₄ .
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Substrate	Chemical shifts (reference CCl ₃ F)
$BmimBF_4$	-145.96 (s) -146.01 (l)
$BmimBF_4$ at anode	-147.15 (l), -143.7 (s), -144.0 (s),
	-144.37 (s) -135 (s), -115 (m), -82 (m)
Upper layer at cathode	-145.7 (trace)
Lower layer at cathode	-146.0 (l)
$C_2H_5OC_2H_5$ condensate	-149.0 (l), -146.49 (s), -146.43 (s)
2 3 2 3	

Literature values: BF₃, 132.7 ppm; BF₄⁻, 149.5 ppm; B₂F₇⁻, 144.2 ppm.¹⁹ BF₃, 131.3 ppm; BF₃·O(CH₂CH₃)₂, 153 \pm 3 ppm; BF₄⁻, 147.5 ppm; F₂, 422.92 ppm.²⁰

^a s: small, m: medium, l: large all refer to the intensity: Negative values refer to high field shifts with respect to CCl₃F.

Table II	¹ H-NMR	data for	electrolysis	of BmimBF ₄ .	
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Substrate	Chemical shifts (δ	: ppm)
BmimBF ₄	8.04 6.91 6.86 3.53 3.25	1.14 0.58 0.15
$BmimBF_4$ at anode	7.86 6.78 3.45 3.15 2.5(s)	1.1 0.5 0.1
Upper layer at cathode	4.99 3.46 2.54 2.23 2	2.09 1.12 0.67
lower layer at cathode	8.30 7.00 6.94 4.81 3.5	8 3.29 1.80
	1.70 1.16 0.61 ().19
$C_2H_5OC_2H_5$	3.59 1.32	
$C_2H_5OC_2H_5$ condensate	3.69 1.15	

cally fluorine should show two sets of peaks, one split into a quartet due to coupling between ¹¹B (I = 3/2) and ¹⁹F, the other split into a septet due to coupling between ¹⁹F and ¹⁰B (I = 3).¹⁸ The intensity of the resonance is due to the different natural abundance of the two isotopes of boron. The reason the splitting was not observed in this system may be due to the viscous nature of the ionic liquid. The chemical shift value agrees with the literature value^{19,20} within 1.5 to 3.5 ppm.

For the ether condensate of the anodic product, ¹⁹F-NMR (Table I) showed a large peak at -149 ppm, which indicated that it was a BF₃ ether condensate. The anodic electrolyte showed a whole range of small peaks from -60 to -150 ppm, presumably due to the fluorinated cation. Therefore the anodic reaction is the oxidation of



Figure 3. ¹H-NMR of (a) $BmimBF_4$ and (b) upper cathodic product after electrolysis.



Figure 4. ${}^{13}C$ -NMR of (a) BmimBF₄ and (b) upper cathodic product after electrolysis.

the anion in the ionic liquid to BF₃ and fluorocarbons.²¹ The literature value of ¹⁹F-NMR for F₂ itself is at 422.92 ppm,¹⁹ which is out of the scale of our NMR machine. ¹H-NMR of the ether condensate (containing free ether) (Table II) moved the chemical shift upfield for the CH₃ group and downfield for the CH₂ group compared to neat ether. This phenomenon is similar to the ¹³C-DNMR behavior observed for the same system.^{22,23} All this showed that BF₃ was produced at the anode. It is likely that the fluorinated cation degraded to CF₄ and other fluorocarbons.²⁴

At the cathode, the ionic liquid displayed two layers. ¹⁹F-NMR of the viscous upper layer showed virtually no resonance peaks, which means $BmimBF_4$ was reduced to neutral molecules without the anion present. The lower layer from the cathodic compartment showed a peak at the same position as BF_4^- , which may indicate that this is the starting material.

¹H-NMR of the cathode upper layer showed the disappearance of resonance above 5 ppm completely (Fig. 3), which indicates reduction occurred at the imidazole ring. The anolyte showed little change in the proton NMR. ¹³C-NMR also supports the idea that the C_2 is reduced into a carbene or saturated carbon, as evidenced by the disappearance of resonance at 134 ppm (Fig. 4, Table III).

The upper layer cathodic electrolyte was analyzed by GC-MS (Fig. 5, Table IV). The BmimBF₄ (Mw 226) mass spectrum was obtained to get insight on the fragmentation pattern of this molecule and the molecules obtained after electrolysis. The base peak is 82, which resulted from the fragmentation of butyl moiety from Bmim⁺ cation. The molecular ion is not observed, the largest m/z value is 124, which is the result of losing the methyl group from Bmim⁺ cation. The anion BF₄⁻ (Mw 87) did not appear. The 97 peak is the result of losing HCN based on the 124 peak, 68 is due to the imidazolium ion, and 55 is due to losing HCN based on 82.²⁵

An iminium salt ($C=N^+$) can undergo two-electron electroreduction producing an anion,^{26,27} which can couple with an electrophile; it can also be involved in a one-electron reduction reaction,

Table III. ¹³ C-NMR data for electrolysis of BmimBF ₄ .				
Substrate	Chemical shifts (6: ppm)			
BmimBF ₄ 13 Upper layer at c 118.02, 117.70, 53.40, 43.47, 43 19.80, 19.58, 13	4.05, 121.66, 120.43, 47.48, 33.91, 29.51, 16.99, 10.94 athode 121.21, 120.98, 120.78, 120.54, 120.37, 120.24 93.03, 90.75, 90.61, 90.35, 79.23, 55.48, 55.38, 55.27, 3.38, 43.25, 43.10, 39.56, 30.10, 28.84, 28.74, 19.85, .52, 13.78			

which then undergoes a free-radical process. In the BmimBF₄ system, there are no free protons available, so no proton uptake is possible. However after the first radical is produced, it can attack the starting material to afford the dimeric radical. In aprotic media, a C—N-Y functional group can undergo cleavage at the N-Y bond, which is the usual reaction.²⁸ In the cathodic electrolysis of Bmim⁺ (Y is carbon in this case), the alkyl group may thus be cleaved. If a carbene is produced, coupling between the same or different carbenes may occur producing different dimers, or even oligomers considering the viscous nature of the upper layer product. As the ¹H and ¹³C-NMR showed the carbon-carbon double bond is intact, there still exists the C₄=C₅ group in the dimers.

There is considerable evidence for the formation of carbenes from dialkylimidazolium salts. Treatment with *t*-BuOK has been shown to produce *t*-butanol, the K⁺ salt of the anion and the liquid carbene²⁹ while reaction with selected zero-valent metal complexes can lead to metal-carbene complexes.³⁰

Electrode reactions.—Based on the above analysis, the following solvent electrode reactions are proposed. At the anode

$$BF_4^- - e \to BF_3 + 1/2F_2$$
 [1]

$$BF_3 + BF_4^- \to B_2F_7^-$$
^[2]

$$F_2 + Bmim^+ \rightarrow fluorocarbons$$
 [3]

At the cathode



Table IV.	GC-MS	analysis	of	the	upper	layer	cathodic	electro-
lyte.								

Retention time (min)	Highest m/z	Base peak	Possible structure
5.00	112	112	Carbon lost from butylimidazole
6.37	168	125	?
7.50	154	98	Coupling of methylimidazole and imidazole
8.77	172	72	Dimer of methylimidazole
12.49	281	238	Dimer of butylmethylimidazole
14.52	254	143	?



Figure 5. TIC of upper layer cathodic electrolyte of $BmimBF_4$ after electrolysis.



In conclusion, BF_4^- oxidizes to BF_3 and fluorocarbons at the anode while $Bmim^+$ undergoes dimerization and dealkylation reactions at the cathode after being reduced to a carbene.

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