We report the easy preparation of high purity EMIBF$_4$ and EMI(CF$_3$SO$_3$) room-temperature ionic liquids, where EMI$^+$ is 1-ethyl-3-methylimidazolium. The ionic liquids prepared by this new procedure are estimated from electrochemical analysis to be 99.5 to 99.9% pure. Importantly, no halides were detected electrochemically, thus this synthesis provides an inexpensive, environmentally benign route to these important air-stable ionic liquid solvents.

INTRODUCTION

Air-stable, room-temperature ionic liquids have recently been demonstrated as exciting new solvents for photovoltaics, homogeneous catalysis, and electrochemical studies. These solvents are composed of a 1,3-dialkylimidazolium cation and typically a perfluoro anion, such as PF$_6$-, SbF$_6$-, BF$_4$-, CF$_3$SO$_3$-, or N(CF$_3$SO$_2$)$_3$. Synthesis of these materials have involved direct chemical reaction, metathesis, and silver halide precipitation. These synthetic routes suffer from a variety of limitations including: (i) difficulty in preparing final products of acceptable purity, (ii) the high cost of precursor reagents, (iii) negative environmental impact of reaction byproducts, and (iv) difficulty in performing large scale reactions. It has been particularly challenging to prepare halide-free EMIBF$_4$ and EMI(CF$_3$SO$_3$) (EMI$^+$ = 1-ethyl-3-methylimidazolium) through the AgCl precipitation route, where AgBF$_4$ and Ag(CF$_3$SO$_3$)$_2$ are used in the synthetic procedures. We report here a facile route to these versatile liquids using the inexpensive and safe NH$_4$BF$_4$ and NH$_4$(CF$_3$SO$_3$)$_2$ salts as the sources for the ionic liquid anions.

The preparation of EMIBF$_4$ involves the direct combination of EMICl and NH$_4$BF$_4$ in acetone and relies on the insolubility of the metathesis product NH$_4$Cl in this solvent. Both EMICl and NH$_4$BF$_4$ are slightly soluble in acetone and so the reaction proceeds by the following steps.

\[
\text{EMICl(s)} \leftrightarrow \text{EMI}^+ + \text{Cl}^- \quad (1)
\]
\[
\text{NH}_4\text{BF}_4(s) \leftrightarrow \text{NH}_4^+ + \text{BF}_4^- \quad (2)
\]
\[
\text{NH}_4^+ + \text{Cl}^- \rightarrow \text{NH}_4\text{Cl(s)} \quad (3)
\]
The final EMIBF$_4$ ionic liquid was recovered by filtration of the NH$_4$Cl and subsequent removal of the acetone solvent using a rotary evaporator. Substitution of NH$_4$(CF$_3$SO$_3$) for NH$_4$BF$_4$, yielded the corresponding EMI(CF$_3$SO$_3$) ionic liquid. Typical preparations for EMIBF$_4$ and EMI(CF$_3$SO$_3$) are described in the following paragraphs.

**EXPERIMENTAL**

**EMIBF$_4$ Preparation** - The reaction was performed in a 250-ml heavy-walled, glass storage bottle (Ace Glass) fitted with a #25 threaded Teflon cap. 10.7714 g of EMICl, prepared as previously described, was weighed under Ar in a Vacuum Atmosphere glove box, removed from the glove box, and added to 100 ml of acetone. Next, 7.683 g of NH$_4$BF$_4$ (Alfa Aesar, 98%) was added to the acetone reaction mixture. Both solid reactants were only slightly soluble in acetone. A stirbar was added to the slurry, and the bottle was capped. After 3 days of vigorous stirring at room temperature, the reaction bottle was opened, and the insoluble NH$_4$Cl methysis product was removed by filtration in the air. To remove trace organic impurities, approximately 1 g of neutral alumina (Brockmann I, standard grade, Aldrich) was added to the acetone filtrate. After stirring for two hours, the alumina was filtered from the solution, and the acetone was removed by rotoevaporation. The final colorless and odorless EMIBF$_4$ product was subsequently dried under vacuum at 120 °C for 6 hours, giving a final yield of 85%.

**EMI(CF$_3$SO$_3$) Preparation** - The synthesis of EMI(CF$_3$SO$_3$) was similar to that described for the preparation of EMIBF$_4$ with the exception that NH$_4$(CF$_3$SO$_3$) was used in place of NH$_4$BF$_4$. Therefore, 10.0 g of NH$_4$(CF$_3$SO$_3$) (99%, Aldrich) was added to 100 ml of acetone containing 8.795 g of EMICl, and the mixture was vigorously stirred for 3 days at room temperature. The NH$_4$Cl was removed by filtration, and the acetone filtrate was treated with neutral alumina. After filtering the alumina and rotoevaporation of the acetone solvent, the EMI(CF$_3$SO$_3$) ionic liquid product was dried under vacuum for 12 hours at 120 °C, giving a final yield of 95%.

**Electrochemical Evaluation of EMIBF$_4$ and EMI(CF$_3$SO$_3$)** - Purity analysis was performed using staircase cyclic voltammetry collected with a computer controlled EG&G PARC Model 273A Potentiostat/Galvanostat. A 1.6-mm diameter Pt disk electrode (Bioanalytical Systems) was used as the working electrode. The reference electrode consisted of an aluminum wire immersed in a 1.5:1.0 acidic AlCl$_3$:EMICl chloroaluminate melt contained in a separate fritted compartment, and the counter electrode was an aluminum wire immersed directly in the ionic liquid analyte. A preparation of EMIBF$_4$ was separated into two equal portions immediately after removal of NH$_4$Cl by filtration. One of the portions was treated with neutral alumina prior to acetone removal by rotoevaporation, while the other portion was rotoevaporated without any alumina treatment. Both EMIBF$_4$ products were vacuum dried separately and transferred to a glove box under an inert Ar atmosphere.
Staircase cyclic voltammograms recorded at 200 mV s⁻¹ for the alumina-treated EMIBF₄ (curve A) and the untreated EMIBF₄ (curve B) are shown in Figure 1. The irreversible reduction wave at -0.8 V in curve B is attributed to the presence of NH₄⁺. This reduction wave is not observed in curve A, i.e., the alumina treatment removes the NH₄⁺ impurity. The small oxidation wave at -0.3 V in both curves has been assigned to the oxidation of the EMI⁺ reduction product. Assuming NH₄⁺ undergoes a one-electron reduction with a diffusion coefficient of 5 x 10⁻⁷ cm² s⁻¹, the 50 µA cathodic current in curve B corresponds to an NH₄⁺ concentration of 30 mM. The inherent ion concentration for EMIBF₄ is ca. 6.3 M; therefore, the untreated EMIBF₄ is 99.5% pure. The cathodic currents in curve A for the alumina-treated EMIBF₄ are < 2 µA, corresponding to < 2 mM impurities and to a purity in excess of 99.97%.

The EMI(CF₃SO₃) prepared from EMICl and NH₄(CF₃SO₃) displayed a 4.2 V electrochemical window and had an estimated NH₄⁺ concentration of 30 mM after treatment with alumina. Therefore, EMI(CF₃SO₃) can be prepared by this method with a purity of at least 99.95%.

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Figure 1 Staircase cyclic voltammograms showing anodic and cathodic scans (200 mV s\(^{-1}\)) at Pt in alumina-treated (curve A) and untreated (curve B) EMIBF\(_4\).