Facile synthesis and characterization of 1-ethyl-3-methylimidazolium fluoride ionic liquid

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Abstract. 1-ethyl-3-methylimidazolium fluoride ([EMIm]F) was synthesized by a facile route via an anion metathesis process. The structure of [EMIm]F was characterized by Fourier transform infrared and Raman spectroscopy, mass spectrometry, as well as nuclear magnetic resonance spectroscopy. The results show that imidazole ring structure is not destructed during the synthesis process, and the disassociated [EMIm]⁺ and [(EMIm)₂F]²⁻ ions are detected in [EMIm]F. It has a potential widow with about 1.80V and shows potential application for reactive metals electrodeposition.

1. Introduction

Ionic liquids (ILs) are composed of organic cations and organic or inorganic anions [1]. Due to the weak binding energy between ions, ILs can be in a liquid state even at room temperature. Therefore ILs are also called low-temperature molten salts. Liquid ethyl ammonium nitrate ((C₂H₅NH₃)NO₃) [2], and 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIm][BF₄]) with low melting point were the first ILs synthesized [3]. ILs has excellent physicochemical properties such as thermal stability, wide electrochemical window, low melting point and high ionic conductivity. The excellent properties make them attractive in a range of applications including catalysis [4], electrochemistry [5], synthesis [6], separation [7,8], and as solvent [9]. The most significant application is metal electrodeposition [10-12]. Ionic liquids are regarded as green materials and expected to be potential substitutes of high temperature molten salts for aluminium production and recycling [13].

For this in general, metal chlorides dissolved in ILs are used for the electro-deposition of the respected metal on the cathode, whilst, hazardous gas chlorine is formed at the anode. In order to avoid chloride evolution, metal oxide can be used instead of chlorides. In this case, the overall reaction can be characterized by formation of metal and oxygen on the cathode and anode, respectively. The utilization of metal oxides is also challenging because of their poor solubility in molten chlorides. By contrast, the solubility of metal oxides in molten fluorides is higher generally. For example, the solubility of Al₂O₃ in NaF-AlF₃ melts is much greater than that in NaCl-AlCl₃ melts. Thus, the fluoride ionic liquids have
been considered as promising green electrolytes which can dissolve more metal oxides. Besides, compared to the traditional metal production processes, energy consumption of metal generation by electrodeposition in ionic liquids can be significantly reduced due to the low temperature.

Due to a strong C-F bond in alkyl fluorides, the imidazolium fluorides can not be synthesized by the quaternization of N-alkylimidazoles with alkyl fluorides [14]. Currently, the mainly methods to synthesis fluoride ionic liquids are electrochemical fluorination and chemical fluorination. However, the purity of product synthesized by electrochemical fluorination is low [15]. Alternatively, F$_2$[16], HF [17], Et$_3$N-3HF [18], ammonium fluoride [19] and metal fluoride [20,21] are used in chemical fluorination process. Unfortunately, chemical fluorination process can hardly be applied in industrial production for the reason that high quality equipment and high production costs are required and both F$_2$ and HF are highly toxic. In this study, a facile process is presented to synthesize high-purity [EMIm]F ionic liquid with a green raw material and its structure were characterized by various techniques.

2. Materials and Methods

2.1. Materials

1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) with 99% of purity and 1-ethyl-3-methylimidazolium bromide ([EMIm]Br) with 99% of purity were provided by Lanzhou Institute of Chemical Physics. Silver fluoride with 98% of purity and analytical grade silver nitrate were purchased from Aldrich. Analytical grade sodium chloride, ethyl acetate and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without further purification.

2.2. Synthesis of [EMIm]F

The reaction principle of synthesizing [EMIm]F from chloride or bromide is based on the different solubility of silver halide. The synthesis procedure of [EMIm]F is as follows. Firstly, 10g of [EMIm]Cl and 8.8g of AgF were dissolved in 25mL and 20mL of distilled water respectively. Secondly, the two solutions were mixed. The white precipitate was observed, which indicated that the metathesis reaction began rapidly. The mixed solution was kept for 24 hours under stirring. Subsequently, the liquid was separated from precipitate by filtration. The filtrate was dried for 48 hours under vacuum condition and a viscous liquid [EMIm]F was obtained. In order to check the purity of [EMIm]F, two samples of the final product were titrated by AgNO$_3$ and NaCl, respectively. No precipitation indicated Cl$^-$ and Ag$^+$ ions were removed completely.

The synthesis principles and process are similar with that described above when using [EMIm]Br instead of [EMIm]Cl.

2.3. Characterization of [EMIm]F

The infrared spectra were recorded on a Fourier transform infrared spectrometer(ALPHA) in the glove box. Raman spectra were obtained by a HR800 Raman spectrometer (Horiba Jobin Yvon) that utilized a 488 nm HeNe laser, 300μm of slit width and wavenumber range 200-4000cm$^{-1}$.The $^1$H-, $^{13}$C- and $^{19}$F-NMR spectra were recorded on a Bruker Avance III 400M nuclear magnetic resonance spectrometer. $^1$H-NMR used acetone (CH$_3$COCH$_3$) as solvent and tetramethysilane [(CH$_3$)$_4$Si] as the internal standard. $^{13}$C-NMR used chloroform (CDCl$_3$) as solvent and tetramethylsilane [(CH$_3$)$_4$Si] as internal standard. $^{19}$F-NMR used chloroform (CDCl$_3$) as solvent and trifluoroacetic acid [CF$_3$COOH] as the internal standard. Mass spectrometry was adopted on a 4000 QTRAP mass spectrometer (Applied Biosystems) to examine the charge-mass ratio. The cyclic voltammogram was conducted on Autolab PGSTAT30 potentiostat equipped with GPES software.

3. Results and Discussion

3.1. Yield of [EMIm]F
The yield is calculated through dividing the actual mass by the theoretical mass based on reaction equation in Fig. 1. The results show that the yield of [EMIm]F can reach as high as 98.00% from [EMIm]Cl and 97.97% from [EMIm]Br.

\[
\begin{align*}
\text{[EMIm]X}^{-} + \text{AgF} & \rightarrow \text{[EMIm]F} + \text{AgX} \\
(X=\text{Cl} \text{ or Br})
\end{align*}
\]

**Figure 1.** Reaction process and products of [EMIm]F obtained at different temperatures: (A)20°C, (B) 50°C, (C) 60°C, (D) 70°C, (E) 75°C

The appearance of [EMIm]F obtained at different temperatures is shown in Fig. 1(A-E). [EMIm]F is a viscous liquid after being dried under vacuum condition. The colors become dark gradually as the temperature increases. It is colorless transparent when it is synthesized at 20 °C. However, its color is pale yellow at 50°C, yellow at 60°C, brownish red at 70°C, and dark brown at 75°C, respectively.

### 3.2. Structure characterizations of [EMIm]F

FTIR and Raman spectra of [EMIm]Cl and [EMIm]F were recorded to study the molecular structure variation.

FTIR spectra of [EMIm]Cl and [EMIm]F are shown in Fig. 2(A). The detailed vibrational data and their assignments of [EMIm]F are summarized in Table S1. The vibrational data of EMIm⁺ are consistent with other works [22, 23]. The main vibrational peaks of EMIm⁺ are observed in both of spectra of [EMIm]Cl and [EMIm]F. The peaks at 3045 cm⁻¹, 1570 cm⁻¹, 1172 cm⁻¹ and 648 cm⁻¹ are attributed to the stretching vibration of C-H, C=C in aromatic ring and stretching, out of plane vibration of C-N in the branched chain, respectively. For [EMIm]F, it is worthy of note that a broad peak at 3400 cm⁻¹ is attributed to the stretching vibration of H-O, which indicate the existence of water molecule and hydrogen bonging between fluoride anion [14, 24].

**Figure 2.** FTIR (A) and Raman spectra (B) of [EMIm]Cl and [EMIm]F
Table 1. Vibrational data and assignments of [EMIm]F

| IR (cm⁻¹) | Raman (cm⁻¹) | Assignment            |
|-----------|--------------|-----------------------|
| 3165 (w)  | v(aro C-H)   |                       |
| 3138 (w)  | v(aro C-H)   |                       |
| 3045 (s)  | 3065 (m)     | v(aro C-H)            |
| 2973 (s)  | 2981 (vs)    | v(ali C-H)            |
|           | 2953 (vs)    | v(ali C-H)            |
| 2863 (m)  | v(ali C-H)   |                       |
| 2839 (m)  | v(ali C-H)   |                       |
| 1699 (vw) |               | R(aro C-H)            |
| 1570 (s)  | 1567 (w)     | v(C=), v_{as}(ring)   |
| 1454 (m)  | 1456 (m)     | δ_{as}(ali)           |
| 1436 (m)  | 1418 (s)     | δ(ali), v(ring)       |
| 1388 (w)  | 1381 (m)     | δ_{sym}(ali), v(ali), v_{as}(ring) |
| 1332 (w)  | 1334 (s)     | v(C_{ali}-N)          |
| 1252 (vw) | 1257 (w)     | r(aro C-H)            |
| 1172 (vs) |               | v(C_{ali}-N), r(ali)  |
| 1117 (w)  | 1124 (m)     | r(ring C-H)           |
| 1093 (w)  | 1092 (m)     | r(ring C-H), r(ali)   |
| 1029 (vw) | 1026 (m)     | δ(ring), breathing, v(C_{ali}-N) |
| 958 (vw)  | 962 (w)      | γ(aro C-H)            |
| 891 (m)   |              |                       |
| 795 (s)   | r(ali C-H)   |                       |
| 697 (w)   | 703 (w)      | v(C_{ali}-N)          |
| 648 (s)   |              | γ(C_{ali}-N), γ(aro C-H)    |
| 598 (w)   |              | v(C_{ali}-N)          |

Raman spectra of [EMIm]Cl and [EMIm]F are shown in Fig. 2(B). The Raman peaks and their assignments are also summarized in Table S1. Compared with [EMIm]Cl, the intensity of Raman peak at 1270-1500 cm⁻¹ in [EMIm]F significantly enhanced. It indicates that fluoride ion strengthened the stretching vibration of C-N, symmetric deformation and bending stretching vibration of -CH₃. The reason is that the smaller radius of fluoride ion enhances its attractive force to imidazole cation.

FTIR and Raman spectra of [EMIm]F indicates that the molecular structure of EMIm⁺ was kept in good condition during the synthesis procedure starting from [EMIm]Cl.
Figure 3. Mass spectrum (A), $^1$H (B), $^{13}$C (C) and $^{19}$F (D) NMR spectra of [EMIm]F

Figure 3(A) shows the mass spectrum of [EMIm]F. Two peaks are detected in mass spectrum. The peak at m/z=111 is assigned to the imidazole cation ([EMIm]$^+$) while the peak at m/z=241.2 is assigned to [EMIm]$^2F^+$ cation. It is indicated that there are two cations ([EMIm]$^+$ and [EMIm]$^2F^+$) existing in [EMIm]F. The [EMIm]$^+$ and [EMIm]$^2F^+$ cations are probably produced by the following dissociation reaction of [EMIm]F molecules.

$$3[EMIm]F \rightarrow [EMIm]^+ + [EMIm]^2F^+ + 2F^-$$ (1)

In order to check the further molecular structure of [EMIm]F, $^1$H, $^{13}$C and $^{19}$F NMR spectra were applied, respectively. $^1$H-NMR spectrum of [EMIm]F is shown in Fig. 3(B). Considering the chloroform would shield the peak at $\delta=10.14$ ppm because of the fluorine atoms, the acetone was applied as the solvent in the experiment. The peaks are at positions of $\delta=10.14$ppm(s,1H), $\delta=7.79$ppm(s,1H), $\delta=7.71$ppm(s,1H), $\delta=4.42$ppm(q, $J=7.3$Hz,3H), $\delta=4.06$ppm(s,3H), and $\delta=1.55$ppm(t, $J=7.3$Hz,3H) respectively. The letters above have their special meanings: $\delta$ means the shift of peaks compared with the internal standard, s is the symbol of single peak, t is the symbol of triplet peak, q is the symbol of quartet peak, the sign nH means this peak has n number of H atoms, and J is the symbol of coupling constant. As shown in Fig.7, the peak with a number is assigned to the H atom marked with the same number in the molecular structure of [EMIm]F.

Figure 3(C) shows $^{13}$C-NMR spectrum of [EMIm]F. The peaks are at positions of $\delta=123.27$ppm(s), $\delta=121.41$ppm(s), $\delta=77.21$ppm(s), $\delta=44.96$ppm(s), $\delta=36.24$ppm(s), and $\delta=15.46$ppm(s), respectively. The peak with a number is assigned to the C atom at the corresponding positions with the same number in the molecular structure of [EMIm]F.

$^{19}$F-NMR spectrum of [EMIm]F is shown in Fig.3(D). Except the peak of the internal standard CF$_3$COOH, only one peak is shown at the position of $\delta=-1.01$ppm(s, 1F) in NMR spectrum. It is concluded that F atom has only one chemical environment in [EMIm]F.
To summarize, according to all the characterizations above, it can be concluded that [EMIm]F was synthetized successfully. During the procedure, the chemical structure of [EMIm]+ cation was not changed and the chloridion or bromide ion in the raw material was replaced by the fluorion.

3.3. Potential window
Fig. 4 shows the Cyclic voltammogram of three platinum electrodes as work electrode, counter electrode and reference electrode in [EMIm]F ionic liquid. Compared with EMIF·2.3HF ionic liquid [17], a similar potential widow with about 1.80V can be found. It is possible to be used in electrodeposition of reactive metals. The further investigation in our lab will focus on the physicochemical and electrochemical properties of [EMIm]F ionic liquid and its electrochemical application.

![Cyclic voltammogram of [EMIm]F. (WE, CE and RE: Pt, scan rate:10mV/s)](image)

**Figure 4.** Cyclic voltammogram of [EMIm]F. (WE, CE and RE: Pt, scan rate:10mV/s)

4. Conclusions
[EMIm]F was successfully synthesized by an anion metathesis process using [EMIm]Cl or [EMIm]Br and AgF as raw materials. [EMIm]F was characterized by FT-IR, Raman spectroscopy, MS and NMR spectroscopy. The structural characterizations indicate that the chemical structure of [EMIm]+ cation is not changed and the chloridion or bromide ion in the raw material is replaced by the fluorion. [EMIm]F ionic liquid has a potential widow with about 1.80V, which is wide enough for potential application for reactive metals electrodeposition.

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