Syntheses and Physicochemical Properties of New Ionic Liquids Based on the Hexafluorouranate Anion

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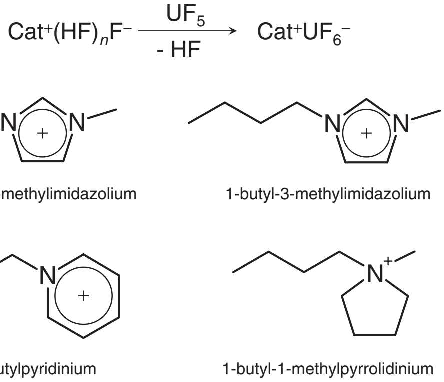
The first syntheses of a series of ionic liquids based on the hexafluorouranate(V) anion are described along with their physicochemical and electrochemical properties. The green room-temperature ionic liquid, 1-ethyl-3-methylimidazolium hexafluorouranate ($EMImUF_6$), exhibits a conductivity of 7.9 $mS\,cm^{-1}$, viscosity of 59 cP, and electrochemical window of 2.3 V at 298 K.

Ionic liquids (ILs) are liquid composed of ionic species. These species have been extensively investigated for uses as electrolytes and reaction media. These liquids are of interest due to their favorable properties including; nonflammability, negligible vapor pressure, wide liquid-phase temperature range, high ionic conductivity, high chemical stability, and/or electrochemical stability.[1] Reports on the syntheses of moisture-stable ILs containing fluoro anions (such as BF_4^-, PF_6^-, and $N(SO_2CF_3)_2^-$) have increased as well as their applications in various fields, replacing conventional aqueous or organic solvents.[2] Another attractive feature of ILs is that their functionalities are tunable by substituting the organic component, functional group, and counter ion. Recently, ILs have attracted interest in the field of nuclear chemistry. This interest is because isotope enrichment using extraction, electrodeposition, or electrophoresis can be achieved with these materials. Previous studies on the radiochemical stability of ILs showed that ILs based on the imidazolium cation are stable enough against radiation doses to be used for such purposes.[3] This letter reports the syntheses and physicochemical properties of a series of novel ILs based on the pentavalent hexafluorouranate(V) anion (UF_6^-).



Scheme 1. Preparation of ILs based on UF_6^- along with the structures of the cations (Cat^+) used in the current work.

Table 1. Thermal and physicochemical properties[a] of the present UF_6 salts measured

	$EMImUF_6$	$BMImUF_6$	$BPyUF_6$	$BMPyrUF_6$
MW	463.2	491.2	488.2	494.3
$\rho/g\,cm^{-3}$	2.43	2.38	—	—
T_m/K	284	n.d.	335	n.d.
T_g/K	n.d.	189	n.d.	n.d.
T_d/K	576	577	511	613
η/cP	59	110	—	—
$\sigma/mS\,cm^{-1}$	7.9	3.3	—	—

[a] MW: molecular weight, T_m: melting point, T_g: glass-transition temperature, T_d: decomposition temperature, ρ: density at 298 K, η: viscosity at 298 K, σ: ionic conductivity at 298 K, n.d.: not detected.

Scheme 1 shows the synthetic route for UF_6^- salts and the structures of the cations used in the current work: 1-ethyl-3-methylimidazolium (EMIm), 1-butyl-3-methylimidazolium (BMIm), 1-butylpyridinium (BPy), and 1-butyl-1-methylpyrrolidinium (BMPyr). The present synthetic method shows the fluoro acid–base reaction between fluorohydrogenate anions and UF_5 (cf. Supporting Information, SI),[4] which has been previously reported for several fluoro complex salts using a fluorohydrogenate IL as a precursor.[5,6] A low halide ion or water content is realized using this method. In this reaction, no sign of decomposition of the organic cations was observed, although UF_5 is a moderate oxidizer. The resulting salts are a green liquid ($EMImUF_6$ and $BMImUF_6$) or green solid ($BPyUF_6$ and $BMPyrUF_6$) at room temperature. The room-temperature ionic liquid, $EMImUF_6$, formed solid, indicating its unstability against hydrolysis. Raman and IR spectroscopy for the obtained salts identified the octahedral UF_6^- ion in the region between 606–610 cm^{-1} for the Raman active ν_1 mode, 192–194 cm^{-1} for the Raman active ν_5 mode and in the region between 515–517 cm^{-1} for the IR active ν_3 mode (cf. SI).[4,7,8] The absence of an absorption band between 3000 and 3100 cm^{-1} suggests that there is no strong hydrogen bonding between the imidazolium ring proton and the anion.

Table 1 summarizes the thermal and physicochemical properties at 298 K of $EMImUF_6$, $BMImUF_6$, $BPyUF_6$, and $BMPyrUF_6$. The two imidazolium-based salts, $EMImUF_6$ and $BMImUF_6$, are room-temperature ILs, whereas the pyridinium-based salt, $BPyUF_6$, melts at 335 K. Although the nonaromatic cation-based $BMPyrUF_6$ does not exhibit a melting point, it shows a crystal–plastic crystal phase transition at 340 K with a small enthalpy change, followed by decomposition at 613 K without melting (cf. SI).[4] As shown in previous studies,[9] the plastic crystal phase often appears for alkylpyrrolidinium cations due to the high rotational freedom of the cation.

Figure 1 shows Arrhenius plots of the viscosity and ionic conductivity of $EMImUF_6$. The ionic conductivity increases with decrease in viscosity. In the narrow temperature range (298–328 K), both the viscosity and ionic conductivity have a linear relationship. The Walden plot where the logarithmic re-

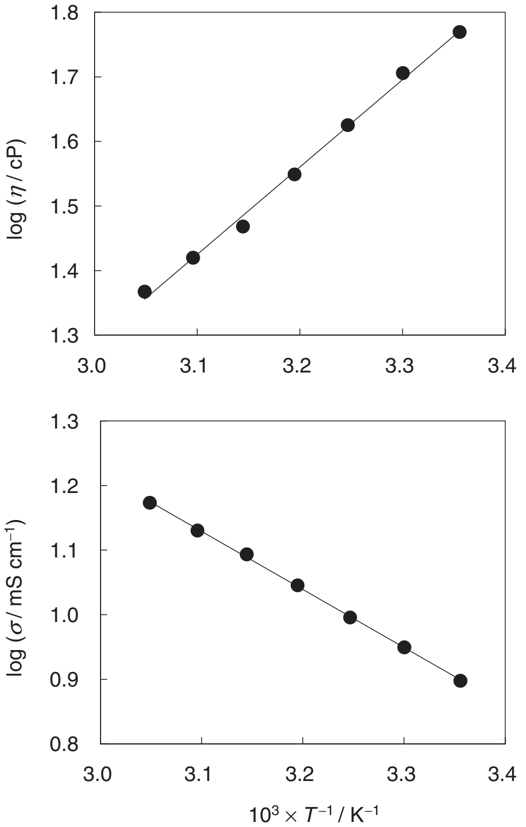


Figure 1. Temperature dependence of viscosity (η) and ionic conductivity (σ) for $EMImUF_6$.

ciprocal molar conductivities of ILs composed of dialkylimidazolium cations and fluoro anions are plotted against their logarithmic viscosities, and the value for $EMImUF_6$ does not deviate from the general trend. This suggests that the mechanism of diffusion of the ionic species in $EMImUF_6$ is similar to the other ILs and that the viscosity dominates the ionic conductivity (cf. SI).[4]

The electrochemical window of $EMImUF_6$ measured using a glassy carbon working electrode is shown in Figure 2. The anode and cathode limits of $EMImUF_6$ are at +1.4 and −0.9 V (vs. Ag^+/Ag), respectively. The anode limit of $EMImUF_6$ is close to those for the other $EMImMF_{m+1}$ ionic liquids (+1.4 V for $EMImBF_4$, +1.5 V for $EMImNbF_6$, $EMImTaF_6$, and $EMImWF_7$),[6] which results from oxidative decomposition of EMIm. The cathode limit for $EMImUF_6$ can be assigned to the reduction of the UF_6^- anion to the lower oxidation state, since the EMIm cation is reductively decomposed at ca. −3 V vs. Ag^+/Ag.[10]

In summary, the syntheses and physicochemical properties of new ILs based on UF_6^- have been reported. The physicochemical properties observed for these ILs are sufficient for electrochemical and chemical processes in the field of nuclear chemistry. Another interesting application may be isotope enrichment using electrophoresis in UF_6^- based ILs.

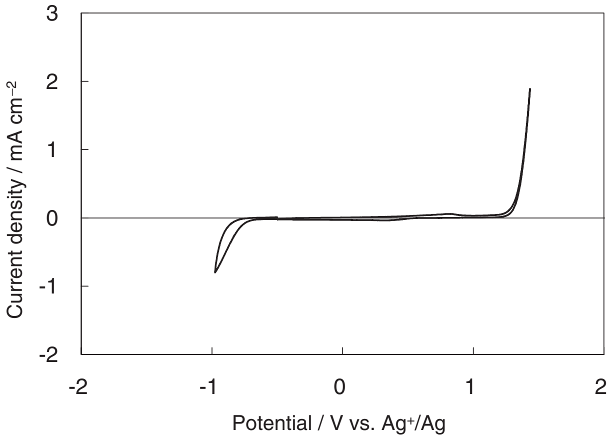


Figure 2. Cyclic voltammogram of a glassy carbon electrode in $EMImUF_6$ at 298 K. Counter electrode: glassy carbon, reference electrode: Ag wire immersed in $EMImBF_4$ containing 0.05 M $AgBF_4$.

References and Notes

1 a) P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071. c) R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792. d) K. R. Seddon, *Nat. Mater.* **2003**, *2*, 363. e) H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley and Sons, Inc., New Jersey, **2005**.

2 a) H. Xue, R. Verma, J. M. Shreeve, *J. Fluorine Chem.* **2006**, *127*, 159. b) R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2000**, *105*, 221. c) K. Matsumoto, R. Hagiwara, *J. Fluorine Chem.* **2007**, *128*, 317.

3 V. A. Cocalia, K. E. Gutowski, R. D. Rogers, *Cood. Chem. Rev.* **2006**, *250*, 755.

4 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

5 a) R. Hagiwara, K. Matsumoto, Y. Nakamori, T. Tsuda, Y. Ito, H. Matsumoto, K. Momota, *J. Electrochem. Soc.* **2003**, *150*, D195. b) K. Matsumoto, R. Hagiwara, Y. Ito, *Electrochem. Solid-State Lett.* **2004**, *7*, E41.

6 K. Matsumoto, R. Hagiwara, R. Yoshida, Y. Ito, Z. Mazej, P. Benkič, B. Žemva, O. Tamada, H. Yoshino, S. Matsubara, *Dalton Trans.* **2004**, 144.

7 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A. Theory and Application in Inorganic Chemistry*, 5th ed., Wiley Interscience, New York, **1997**, p. 218.

8 a) J. Selbin, J. D. Ortego, *Chem. Rev.* **1969**, *69*, 657. b) B. Frlec, H. H. Hyman, *Inorg. Chem.* **1967**, *6*, 2233.

9 a) J. Adebahr, M. Forsyth, D. R. MacFarlane, *Electrochim. Acta* **2005**, *50*, 3853. b) S. Forsyth, J. Golding, D. R. MacFarlane, M. Forsyth, *Electrochim. Acta* **2001**, *46*, 1753.

10 Y. Katayama, S. Dan, T. Miura, T. Kishi, *J. Electrochem. Soc.* **2001**, *148*, C102.

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