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Short communication

# Acidic 1-ethyl-3-methylimidazolium fluoride: a new room temperature ionic liquid

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## Abstract

Reaction of 1-ethyl-3-methyl imidazolium chloride (EMIC) and hydrogen fluoride gives an yellow, involatile liquid, EMIF·2.3HF. The liquid is stable in air and able to be stored in a glass container. The specific conductivity was about 12 S $m^{-1}$ at 298 K. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* EMI; EMIC; EMIF; Ethyl methyl imidazolium; Ionic liquid

## 1. Introduction

EMIC, 1-ethyl-3-methyl imidazolium chloride ($C_6H_{11}N_2Cl$), is now widely employed as a cationic source for low temperature molten salts. The combination of EMIC and aluminum trichloride [1] is the system most extensively studied for practical applications such as organic reactions, batteries and metal depositions [2–7]. Recently, several low temperature ionic liquids have been prepared by combining EMI cation with organic and inorganic fluoride anions [8–11], and their electrochemical behaviors have been investigated [9,11]. In this paper, we report a new ionic liquid, EMIF·2.3HF and its unique properties.

## 2. Experimental

EMIC supplied was dissolved in acetonitrile dried over molecular sieves, and then precipitated from the solution by addition of ethyl acetate. This treatment was performed in a glove box and repeated three times. The purified EMIC was weighed and charged in an FEP (fluoroethylene–propylene copolymer) reaction tube. Large excess anhydrous HF dried over $K_2NiF_6$ was transferred to the reaction tube by condensation through a metal vacuum line. During the reaction at ambient temperature, the evolved gas was occasionally transferred to an IR gas cell with AgCl windows. After the reaction ceases, volatile material was evacuated from the reaction tube. The vacuum attained was $10^{-1}$ Pa at ambient temperatures. The transparent yellow liquid obtained was weighed in the glove box to determine the weight uptake. Elemental analyses were performed at the Laboratory for Organic Elemental Microanalysis of Kyoto University. Raman spectra of the samples were obtained by a BIO-RAD FTS-175C spectrometer using Nd:YAG laser (1200 mW). IR spectra of solid and liquid samples were obtained by a BIO-RAD FTS-155 spectrometer using AgCl crystal disks. Preliminary electrochemical measurements were performed using a platinum working electrode ($1.4\times10^{-4}$ $m^2$ of geometrical surface area), a platinum quasi reference electrode and a tungsten counter electrode, with the aid of Hokuto Denko, HZ-3000 electrochemical measurement system.

## 3. Results and discussion

The reaction started during the temperature elevation after condensation of HF. Gas evolution was observed and the color of liquid turned yellow. Colorless gas sampled from the reaction tube became red when frozen by liquid nitrogen. The IR spectroscopy detected hydrogen chloride. From the weight uptake ($C_6H_{11}N_2F$·2.25HF) and the elemental analysis (C : H : N : F=6.0 : 13.3 : 2.0 : 3.3), the composition of the product was determined to be $C_6H_{11}N_2F$·2.3HF. The reaction is concluded to proceed as follows, similar to the synthesis of acidic tetra-alkylammonium fluorides from

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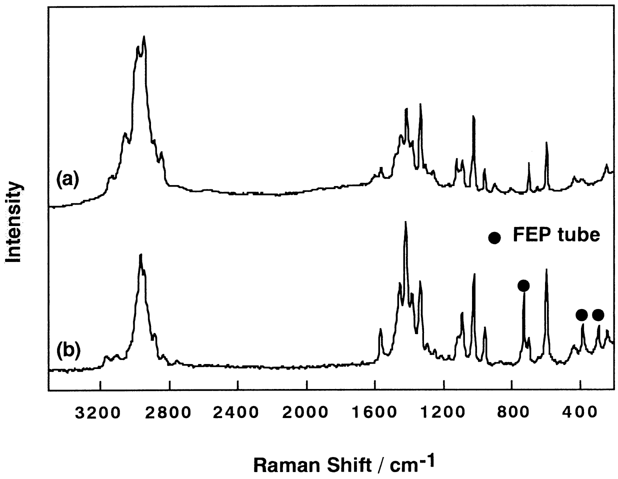

Fig. 1. Raman spectra of EMIC and EMIF·2.3HF: (a) EMIC (solid, glass tube); (b) EMIF·2.3HF (liquid, FEP tube).

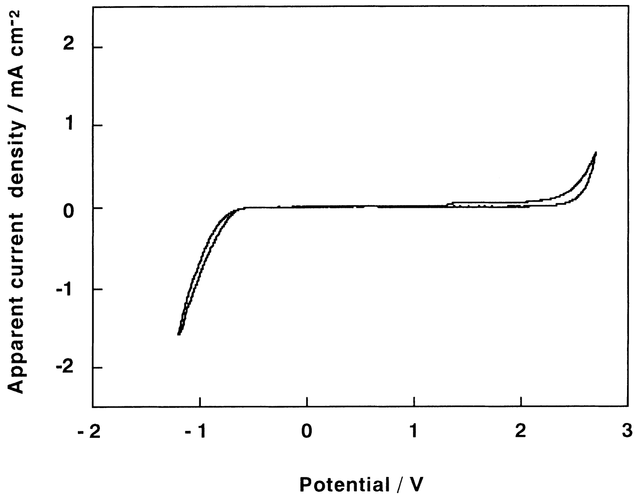

Fig. 3. Cyclic voltammogram of EMIF·2.3HF. WE : Pt, CE : W, QRE : Pt, scan rate 100 mV $s^{-1}$.

their bromides and chlorides [12]:

$$\mathrm{EMICl} + (n+1)\mathrm{HF} \rightarrow \mathrm{EMIF} \cdot n\mathrm{HF} + \mathrm{HCl} \uparrow . \quad (1)$$

Figs. 1 and 2 show the Raman and IR spectra of the reaction product compared with the original EMIC. Peaks of EMI cation are preserved in the spectrum of the reaction product. The new peaks are broad, found at around 490, 1000, 1800 and 2000 $\mathrm{cm}^{-1}$ in the IR spectrum. The pattern resembles those of $H_2F_3^-$ anion ($C_{2v}$) in KF·2HF and $H_3F_4^-$ anion ($D_{3h}$) in KF·3HF, each peak being ascribed to F···F stretching, FHF bending, F–H stretching and combination mode, respectively [13–15]. The IR spectra of $F(HF)_n^-$ ($n$=2–4) are quite similar with each other and the anion type in this liquid cannot be identified unambiguously. However, taking account of the formula experimentally obtained, there is a possibility of coexistence of anions more than one kind in this liquid. The freezing point was determined to be 183 K. Above 323 K, the color of the liquid became darker although the vibrational spectra were unchanged. The liquid does not etch the glass container and the spectrum was unchanged even after exposing the sample to air overnight. The liquid violently reacts with elemental fluorine.

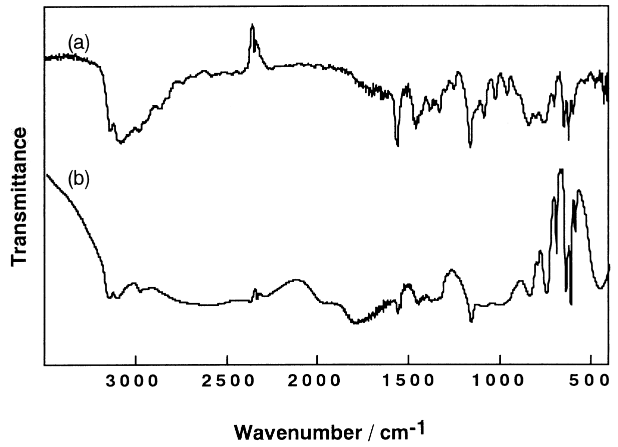

Fig. 2. IR spectra of EMIC and EMIF·2.3HF: (a) EMIC (solid); (b) EMIF·2.3HF (liquid).

Fig. 3 shows the cyclic voltammogram of the platinum electrode immersed in EMIF·2.3HF, indicating that the liquid is electroconductive and possesses a potential window comparable with that of EMIC–$AlCl_3$ system [16]. The cathodic current is ascribed to the reductive decomposition of the EMI cation. Although the anodic reaction is still uncertain, the oxidation of the anions, namely, the fluorine gas evolution is ruled out taking account the reactivity of the liquid against the elemental fluorine. The conceivable reactions are the oxidation of EMI cation and dissolution of the electrode. The electrical conductivity measured by an impedance technique was about 12 S $\mathrm{m}^{-1}$ at 298 K. Further investigation is now under way focusing on the application as an electrolyte for electrochemical processes.

## References

[1] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.

[2] C.L. Hussey, Room temperature molten salt systems, in: G. Mamantov (Ed.), Advances in Molten Salt Chemistry, vol. 5, Elsevier, New York, 1983, p. 185.

[3] J.S. Wilkes, Friedel–Crafts reactions in chloroaluminate molten salts, in: G. Mamantov, R. Marassi (Eds.), Molten Salt Chemistry, NATO ASI series, Series C, Mathematical and Physical Sciences, vol. 202, Reidel, Dordrecht, 1987, pp. 405–416.

[4] G. Mamantov, C.L. Hussey, R. Marassi, An introduction to electrochemistry in molten salts, in: R. Varma, J.R. Selman (Eds.), Techniques for Characterization of Electrodes and Electrochemical Processes, Wiley, New York, 1991, pp. 474–475.

[5] C.L. Hussey, Pure Appl. Chem. 60 (1988) 1763.

[6] C.L. Hussey, The electrochemistry of room-temperature haloaluminate molten salts, in: A. Popov, G. Mamantov, (Eds.), Chemistry of Nonaqueous Solvents, Chapter 4, VCH, New York, 1994, p. 227.

[7] R.T. Carlin, J.S. Wilkes, Chemistry and speciation in room-temperature chloroaluminate molten salts, in: A. Popov, G. Mamantov (Eds.), Chemistry of Nonaqueous Solvents, Chapter 5, VCH, New York, 1994, p. 277.

[8] J.S. Wilkes, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1992) 965.

[9] R.T. Carlin, H.C.D. Long, J. Fuller, P.C. Trulove, J. Electrochem. Soc. 141 (1994) L73.

[10] J. Fuller, R.T. Carlin, H.C.D. Long, D. Haworth, J. Chem. Soc., Chem. Commun. (1994) 299.

[11] J. Fuller, R.T. Carlin, R.A. Osteryoung, J. Electrochem. Soc. 144 (1997) 3881.

[12] I.N. Rozhkov, I.Y. Alyev, Tetrahedron 31 (1975) 977.

[13] A. Azman, A. Ocvirk, D. Hadzi, P.A. Giguaère, M. Schneider, Can. J. Chem. 45 (1967) 1347.

[14] K.M. Harmon, I. Gennick, J. Mol. Str. 38 (1977) 97.

[15] K. Wada, T. Takenaka, S. Hayashi, S. Takeno, JJAP (Suppl.) 2 (1974) 109.

[16] P.R. Gifford, J.B. Palmisano, J. Electrochem. Soc. 134 (1987) 610.