Alkylimidazolium fluorohydrogenates room temperature molten salts

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By the reaction of *N*-alkylimidazolium chlorides or *N*-alkylimidazole with anhydrous hydrogen fluoride (HF), involatile room temperature molten salts (RTMS), XF 2.3HF have been synthesized where X = 1-methylimidazolium (MI) [1,2], 1,3-dimethylimidazolium (DMI), 1-ethyl-3-methylimidazolium (EMI) [1-5], 1-methyl-3-*n*-propylimidazolium (PrMI), 1-*n*-butyl-3-methylimidazolium (BMI) [1,2], 1-methyl-3-*n*-pentyl-imidazolium (PeMI), 1-*n*-hexyl-3-methylimidazolium (HMI) [1,2]. Vacuum stable salts at room temperature exhibit the same composition regardless the type of the cation.

The spectroscopic analyses suggest the existence of oligomeric anions such as $H_2F_3^-$ and $H_3F_4^-$ as main components in these salts [3]. Table 1 shows some physical properties of these RTMS. High specific conductivities, 110 $mScm^{-1}$ and 100 $mScm^{-1}$ for DMIF 2.3HF and EMIF 2.3HF at 298 K [1-5]. Substitution of the proton or the longer alkyl side chains for the ethyl group of the imidazolium cation increases the viscosity and decreases the conductivity. These salts are stable in air and do not etch a Pyrex glass container at ambient conditions. Electrochemical windows of these salts are about 3 V in the case of EMIF 2.3HF [3,4]. The elongation of alkyl side chain on the cation increases the electrochemical windows of these salts.

Low temperature (but not room temperature) melting salts, alkylimidazolium bifluorides, XHF_2, are crystallized from some HF deficient melts prepared by the decomposition of anions at elevated temperatures (in the case of EMI salts, at around 400 K). Figure 1 shows the crystal structure of $EMIHF_2$ (m.p. 324 K) in which the columnar stacking of the cations via hydrogen bonding between one of the ring protons and the π-electrons on the neighboring cations.

These RTMS act as Lewis base against fluoroacids to give some molten fluorometallates without any involatile byproducts. The stoichiometric reaction of EMIF 2.3HF and solid fluorides, NbF_5 and TaF_5, gives new RTMS with similar properties, $EMINbF_6$ and $EMITaF_6$, respectively (Table 2) [7]. Raman spectroscopy revealed the room temperature vacuum stable salt obtained by the reaction of EMIF 2.3HF and excess SbF_5 is not a simple SbF_6^- salt but that containing oligomeric anions such as $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$.

References

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Table 1 Some physical constants of alkylimidazolium fluorohydrogenates XF 2.3HF at 298 K.

Salts	M.W.	Density / gcm^{-3}	Viscosity /cP	Specific conductivity / $mScm^{-1}$
MIF 2.3HF	148	1.20	8.9	60
DMIF 2.3HF	162	1.17	5.1	110
EMIF 2.3HF	176	1.13	4.9	100
PrMIF 2.3HF	190	1.11	-	61
BMIF 2.3HF	204	1.08	19.6	33
PeMIF 2.3HF	218	1.05	-	-
HMIF 2.3HF	232	1.00	25.8	16

Table 2 Some physical constants of $EMINbF_6$ and $EMITaF_6$.

	$EMINbF_6$	$EMITaF_6$
Melting point / K	272	275
Glass transition temperature / K	181	-
Density at 298 K /gcm^{-3}	1.67	2.17
Molar volume at 298 K / cm^3mol^{-1}	190	187
Conductivity at 298 K / $mScm^{-1}$	8.5	7.1
Viscosity at 298 K / cP	49	51

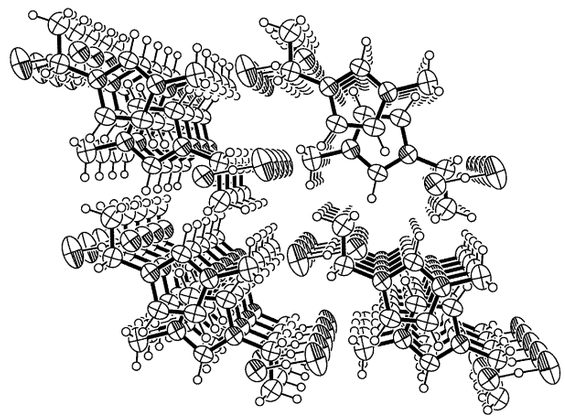

Fig. 1 Perspective view of the structure of $EMIHF_2$ [6].