Air and Water Stable 1-Ethyl-3-methylimidazolium Based Ionic Liquids

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A series of novel air and water stable low melting salts based upon the 1-ethyl-3-methylimidazolium cation (EtMeim+) have been prepared and characterized; two salts, [EtMeim]BF$_4$ and [EtMeim]MeCO$_2$, are liquids under ambient conditions.

Alkylpyridinium (Rpy+) chloroaluminate based ambient temperature ionic liquids have been known since the 1950s,[1] however, it was the discovery of EtMeim+ based chloroaluminate ionic liquids in 1982[2] that afforded the impetus for a dramatic increase in activity in the area. The latter class of compounds exhibits a wider liquidus range and an electrochemical window of >3.0 V and has therefore become of great interest from both an electrochemical[3] and a synthetic perspective.[4] A considerable drawback of ambient ionic liquids concerns the need to protect rigorously the ionic liquids from moisture and other oxide impurities and the tendency of many substrates to react with halometallates. Use of ambient temperature ionic liquids has therefore thus far been limited to a narrow range of organic substrates, typically those that react

desirably with Lewis acids such as Friedel–Crafts substrates.[4] In contrast, there are a plethora of higher melting salts, typically based upon halides, halometallates and more inert anions such as nitrate, sulfate and carbonate, that have been utilized as electrolytes.[5] It occurred to us that were the inertness and facile handling capability of some of the higher melting salts to become feasible under ambient conditions, then the possibilities for applications of ionic liquid media would become greatly enhanced. In this communication we report the preliminary results of a study that has focused upon extending the range of known EtMeim+ salts so as to include
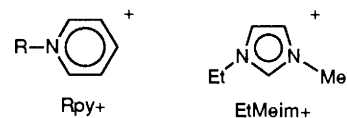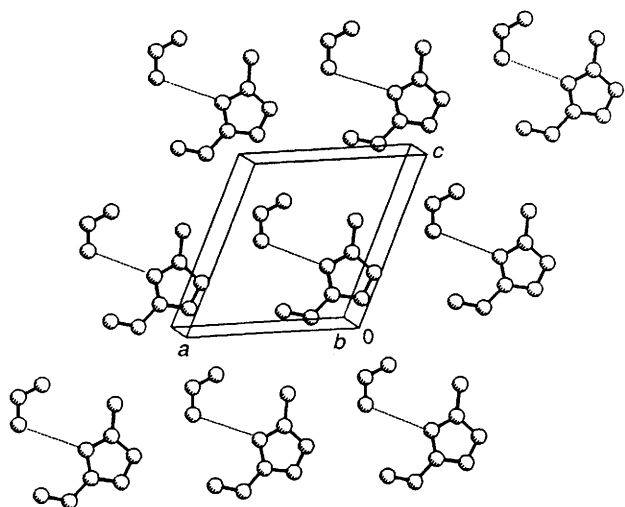
Rpy+   EtMeim+

Fig. 1 View of the *ac* plane in [EtMeim]NO₂. Layers eclipse each other to form an *ababab* structure with an interplane separation of *ca.* 3.4 Å. Closest interionic contact is a C⋯O distance of 3.234(5) Å between position 2 of the im ring and O(2).
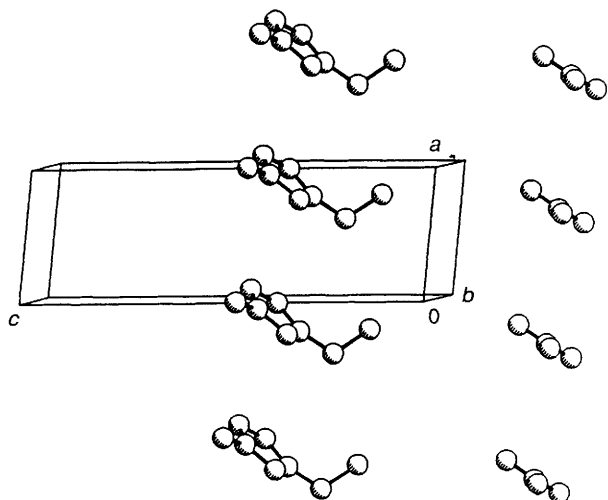

Fig. 2 View of the *ac* plane in [EtMeim]NO₃, which illustrates the stacking of cations and anions. The interplane separation of the plane of the ions corresponds to the *a* axis and is therefore *ca.* 4.5 Å. The closest interionic contact is a C⋯O distance of 3.078(6) Å between position 2 of the im ring and O(2). There are several other contacts within 3.3 Å.

anions which would permit more widespread usage of ionic liquids as both electrolytes and reaction media.

The following salts‡ were prepared quantitatively on the benchtop *via* metathesis of [EtMeim]I and the appropriate silver salt in MeOH or MeOH–H₂O: [EtMeim]NO₃, **1a**, m.p. 38 °C; [EtMeim]NO₂, **1b**, m.p. 55 °C; [EtMeim]BF₄, **1c**, m.p. 15 °C; [EtMeim]MeCO₂, **1d**, m.p. *ca.* −45 °C; [EtMeim]₂-SO₄·H₂O, **1e**, m.p. 70 °C. With the exception of **1e** all salts are hygroscopic but no special precautions are required during synthesis as they may be dried conveniently in a vacuum oven at 80 °C. This is in contrast to higher melting metal based salts which can form thermodynamically stable hydrates that are much more difficult to dehydrate.⁶ Crystals of **1b** and **1e** were obtained *via* cooling a saturated MeCN–Et₂O solution of the salt whereas **1a** was crystallized through slow cooling of the molten salt to room temperature. Compound **1c** supercools to

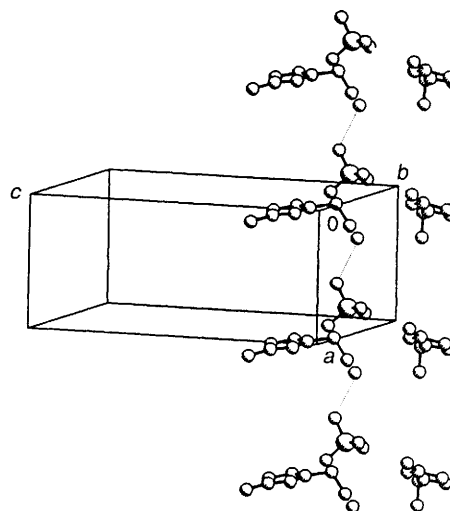‡ Satisfactory microanalysis and NMR spectra were obtained for **1a–e**.

Fig. 3 Cell-packing diagram for [EtMeim]₂SO₄·H₂O illustrating the stacked [EtMeim]⁺ cations. The closest interionic contacts are 3.202(6) and 3.214(7) Å between position 2 of each im ring and sulfate oxygen atoms. The water molecule of solvation bridges sulfate anions, thereby forming an anionic stack parallel to the cationic stack.

at least −20 °C whereas **1d** freezes to a glass at −45 °C although it beomes extremely viscous below −20 °C.

The nature of the EtMeim⁺ cation and how it interacts with various anions has previously been explored in both solution⁷ and solid⁸ phases and *via* theoretical studies.⁹ It is apparent that hydrogen bonding *via* the hydrogen atom at position 2 of the im ring is a common feature of basic ionic liquids (*i.e.* mole fraction of AlCl₃ < 1.0) but what influence this has upon the structure and physical properties of melts and solids remains unclear. In order to evaluate how EtMeim⁺ interacts with the anions chosen for this study the X-ray crystal structures of **1a**, **1b** and **1e** were determined.§ Analysis of the interionic contacts reveals the presence of C–H⋯O hydrogen bonding in all three compounds, with the hydrogen atom at position 2 exhibiting the strongest interactions. Indeed, the C–H⋯O distances are at the short end of the range expected for a C–H⋯O hydrogen bond,¹⁰ being comparable to those exhibited for strong Cl₃CH⋯O hydrogen bonds.¹¹ Cell packing diagrams illustrate that **1b** (Fig. 1) exhibits hexagonal close-packing whereas **1a** and **1e** (Figs. 2 and 3, respectively) pack so that the EtMeim⁺ cations are vertically stacked. A similar stacking of cations was observed in the solid state for [EtMeim]Cl.¹² It is interesting to note that we have not yet encountered similar stacking in related pyridinium or 1,3-

dimethylimidazolium salts.[13] The C–H⋯O hydrogen bonding in the plane of the ions results in a cross-linked 2D network for 1a, an ion pair in the case of 1b and a 3D network for 1e, which has O–H⋯O hydrogen bonding perpendicular to the plane of the ions. The C–H⋯O hydrogen bonding therefore appears strong enough to preclude normal ionic packing but not strong enough to increase significantly the melting points.

It is clear from this study that EtMeim+ is an ideal candidate for general use in ionic liquids. It is of moderate size (thereby lowering lattice energies), its shape appears to promote cation stacking, it is facile and inexpensive to prepare, chemically and electrochemically robust, and can only engage in the thermodynamically weak C–H⋯X hydrogen bonding. We are presently continuing our investigation of 1a–e in the context of media for electrochemistry and synthesis.

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