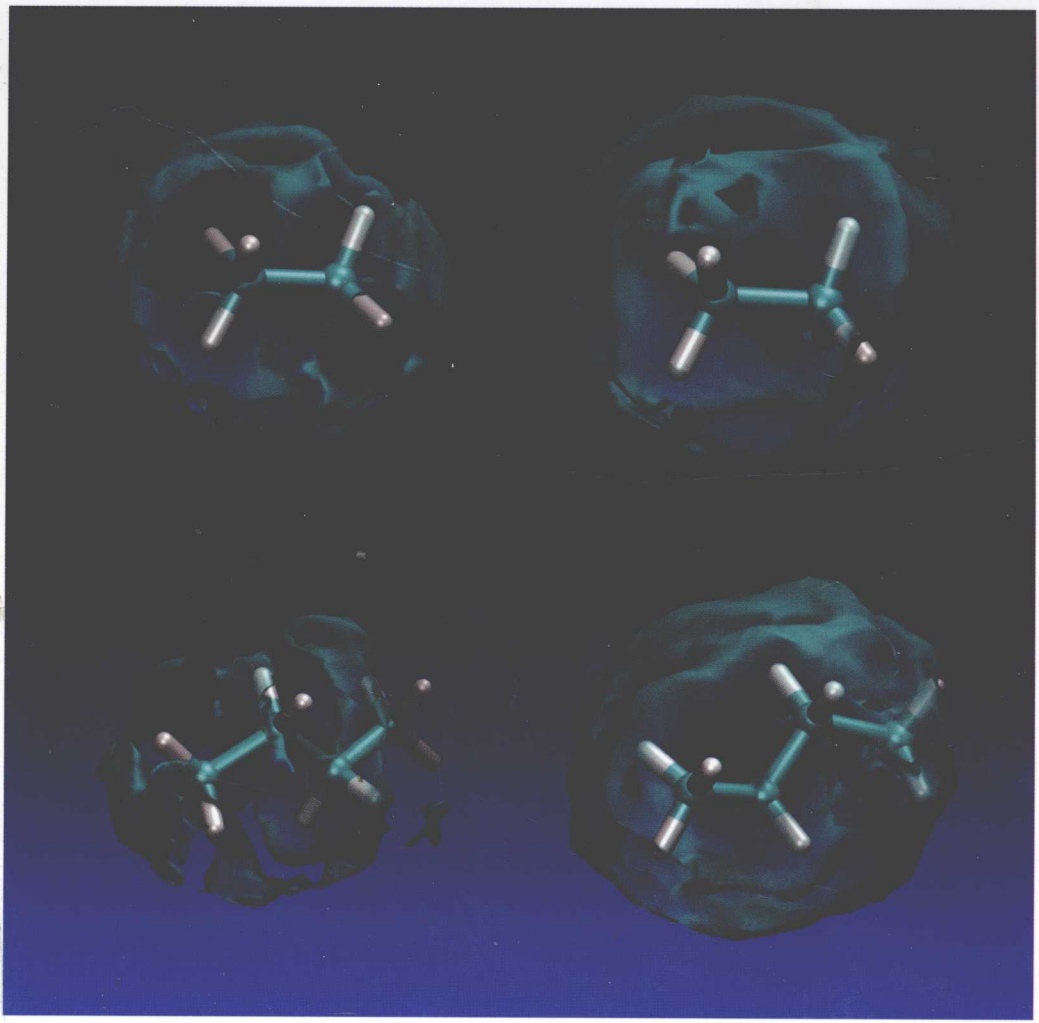
Faraday Discussions Vol 154

Ionic Liquids



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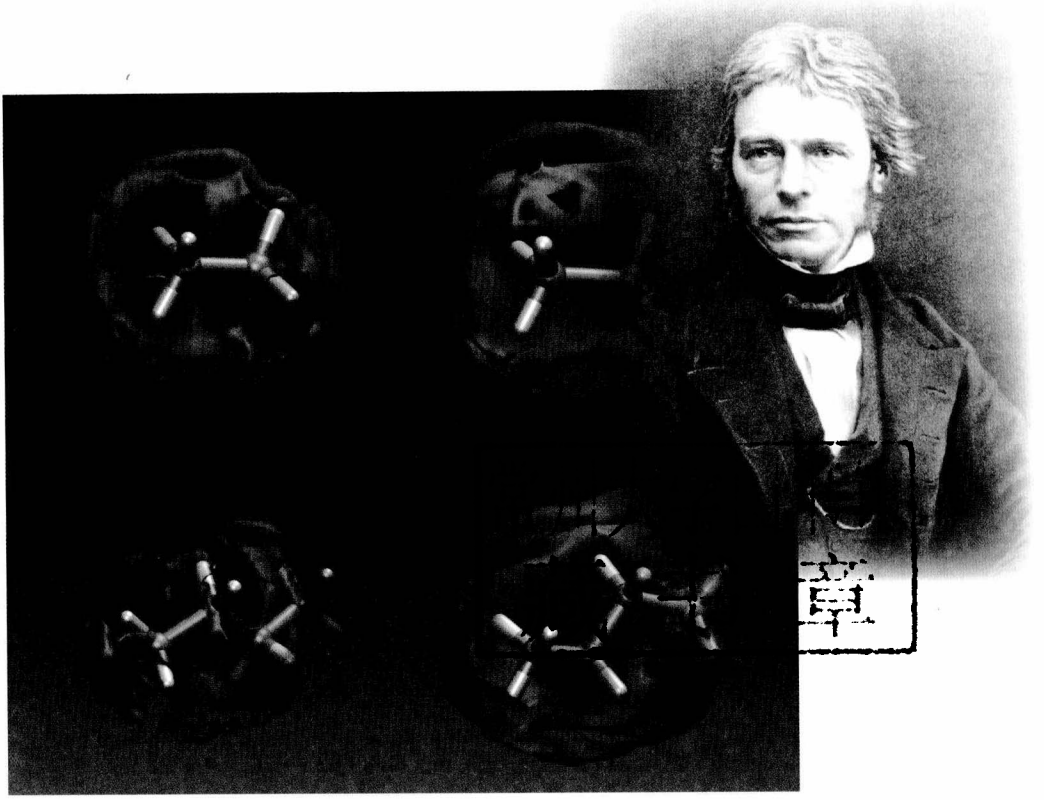
Ionic Liquids

Queen's University, Belfast,
United Kingdom

22–24 August 2011



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Ionic Liquids

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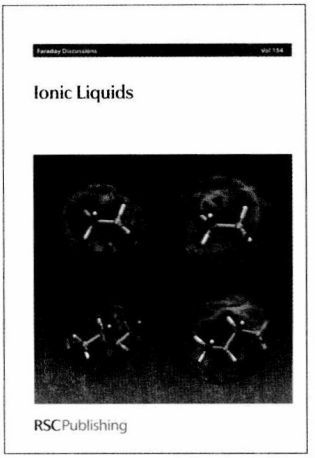

Cover

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The figure shows the spatial distribution functions of the alkyl side chain terminal carbon atoms of the imidazolium cations, in $[C_nC_1Im][Ntf_2]$ ionic liquids, around ethane and butane solutes. Both solutes are solvated in the non-polar domains of the ionic liquids, the first solvation shell being predominantly occupied by the alkyl chains of the cation.

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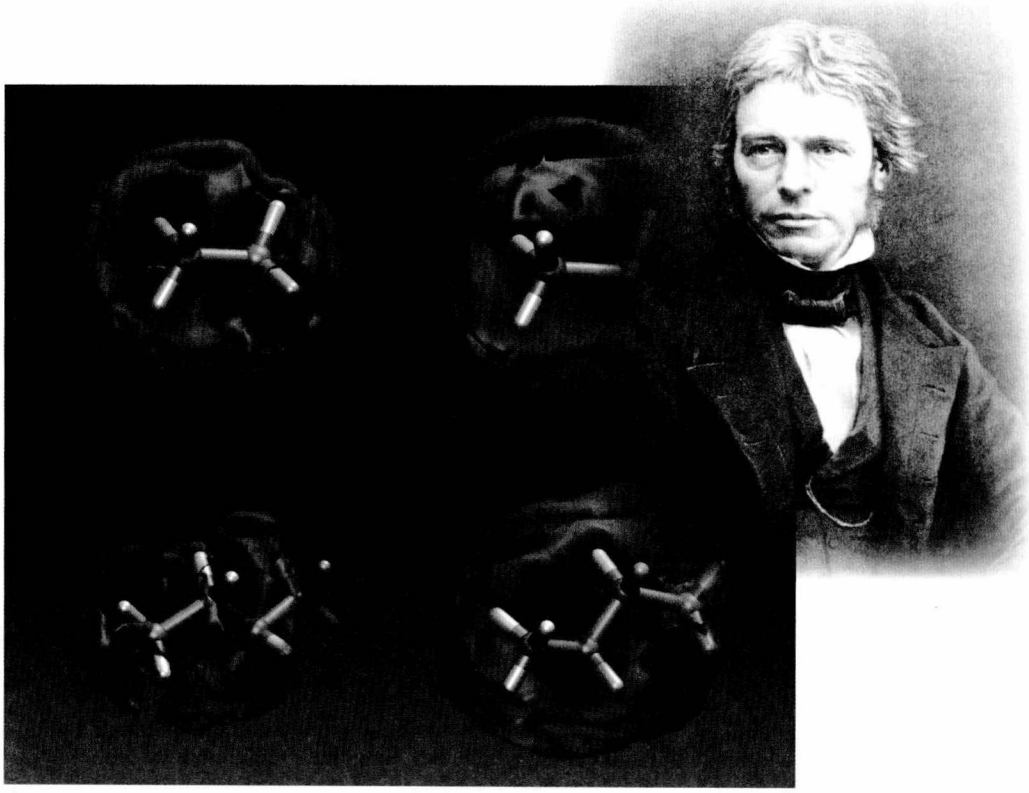

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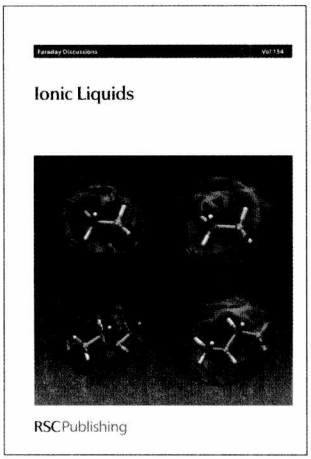

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INTRODUCTORY LECTURE

PAPERS AND DISCUSSIONS

Ionic Liquids: Past, present and future

C. Austen Angell,* Younes Ansari and Zuofeng Zhao

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An overview of the field of low-melting ionic liquids is given from its inception in 1886 through to the present time. The subject is divided into an introductory section that summarizes the early history of the field, and differentiates its subsections, before addressing matters judged of some interest in "pre-surge" and "post-surge" stages of its development, focusing on physicochemical as opposed to the prolific synthetic and industrial aspects in which the author has no competence. We give a final section specifically to protic ionic liquids, which we consider to have particular scientific potential.

A. Introduction

This article is intended to provide some background to the subject of the present Faraday Discussion on Ionic Liquids and, to this end, will consist of three sections after this introduction. The first will be devoted to a short history of the subject intended to show how the present state of enthusiasm for low melting ionic assemblages has arisen out of a diverse background of ionic liquid studies before taking off under its own considerable force of innovation. The second section is intended to provide some understanding of the various reasons for the current state of enthusiasm for the field, and the third section will attempt to give it some additional depth and projection as it enters the stage of a maturing discipline, mostly using examples from the authors' own recent works.

Like all of electrochemistry and ionic liquid physical chemistry, the field started with Humphrey Davy's pioneering work on the electrolytic decomposition of simple molten salts under the influence of an applied dc electric field, to yield the elements that initially had been chemically combined in the salt under study. Davy's studies, collected in his major work,[1] place the investigation of ionic liquids at the very beginning of organized chemical science. They were preceded only by the alchemists' more chaotic studies of molten nitrates and ammonium salts to which no reference will be made here.

Davy worked primarily with the high-melting simple salts. The first person to consciously use an ambient temperature ionic liquid for scientific purposes seems to have been the Nobel Prize-winning physicist, Ramsay, who is reported by Schottenberger and co-workers[2] to have described "syrupy ionic liquids" that he prepared by combination of acids with picoline.[3] Although other early studies are known[2] the first that we will discuss here is the case of ethylammonium nitrate, prepared deliberately for its ionic character by Paul Walden in 1914.[4] It has probably been studied in more detail, and for more purposes, than any other ionic liquid. Walden and his works are important to us because in his earlier studies of aqueous solutions, he had formulated the Walden rule[5] that relates the equivalent conductivity Λ of an ionically conducting liquid to its viscosity η.

$$\Lambda\eta = \text{const.} \tag{1}$$

The rule has provided the basis for a very useful classification of ionic liquids, about which more will be said below.

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Although eqn (1) worked reliably for aqueous solutions the early German school of molten salt chemists, studying low-melting silver salts, found that the rule broke down seriously and needed to be replaced by the "fractional" Walden rule where γ is a constant $0 < \gamma < 1$.

$$\Lambda\eta^{\gamma} = \text{const.} \tag{2}$$

The fractional Walden rule implied that the Arrhenius activation energy for conductivity was lower than that for viscosity, which was readily interpreted in terms of the smaller silver ion slipping through the quasilattice of the larger halide ions, this picture being particularly clear in the case of the silver iodide which was a good conductor even in its crystalline state at temperatures near the melting point. Such violations of the Walden rule are now referred to as "superionic" behavior, and are much sought after in the field of glassforming ionic liquids (where solid electrolytes are the prize) and particularly protonic ionic liquids (that might serve as fuel cell electrolytes). Some progress in this area will provide the substance of the last section of this article.

The silver salts of the early German studies were low-melting but were not ambient temperature liquids or even liquids with melting points below 100 °C in the sense of the "ionic liquids" that are in focus in most of the papers at this discussion. Inorganic examples of ionic liquids that satisfy this criterion do exist, however, and it would be useful at this point to briefly delineate the types of substances that together make up the sub 100 °C melting subjects of this discussion —liquids that in principle consist only of ions. Here we follow the classification given by the present author[6] in the book edited by Ohno "Electrochemical Aspects of Ionic Liquids" (Chapter 2).

Classes of ionic liquids

1. Aprotic ionic liquids. The majority of ionic liquids, and certainly those responsible for the meteoric rise in the number of publications in this area since the mid-90's, are liquids in which the cations are organic molecular-ions. Examples would be the resonance stabilized alkyl pyridinium and dialklyimidazolium cations that go back to Hurley and Weir[7] in the middle of the last century. They mixed *N*-substituted alkyl and aryl pyridinium halides with various metal chlorides and nitrates and obtained low- liquids with which they performed electrochemical extractions (though they seem to be best known for their efforts on aluminum deposition on which they took the first patents). Hurley and Weir presented the first phase diagram on an aluminum chloride + organic cation halide system, which showed the existence of stable ionic liquids at temperatures of −40 °C (Fig. 1).

Much more recently developed have been the cyclic,[8] and non-cyclic[9,10] tetraalkyl ammonium salts like those with alkylpyrrolidinium cations, and particularly those with ether oxygenated sidechains.[10] Such cations are usually charge-compensated by anions of oxidic character like nitrate perchlorate or more frequently fluorinated-oxidic character like triflate. Among the most common of the latter are the PF_6^-, BF_4^-, triflate (trifluoromethane sulfonate, CF_3SO_3), and bis-trifluoromethanesulfonyl-imide, $(CF_3SO_2)_2N$, or NTf_2) ions. The fluorinated anions are prominent because of the viscosity-lowering reduction of the van der Waals interactions (thanks to the tightly bound, hence unpolarizable, character of the fluorine electrons). The particular success of the NTf_2^- anion, which is quite a large anion, may be due to the feature pointed out by Henderson,[11] namely, that this ion has two isoenergetic forms, hence can add an extra, (and therefore liquid-stabilizing) mode to the configurational entropy.

2. Protic ionic liquids. These are formed by the simple transfer of a proton from pure Brønsted acid to pure Brønsted base. Historically the first ILs made, as noted already, their development in the modern era was spearheaded by the Ohno[12,13] laboratory in Japan. The nature and reversibility of this process establishes a proton

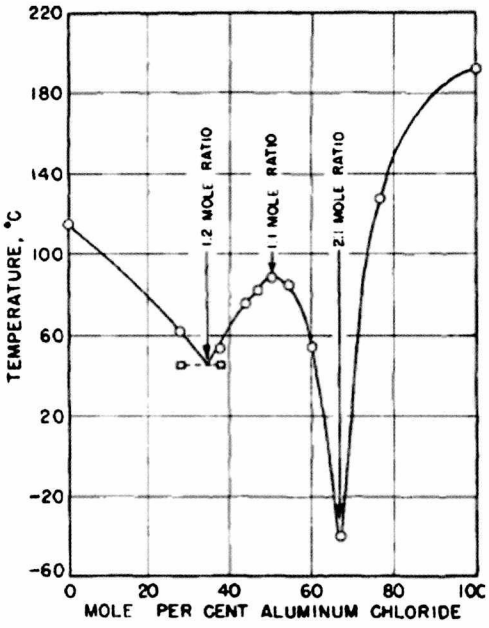

Fig. 1 Phase diagram of the system ethylpyridinium bromide + $AlCl_3$ (from Hurley and Weir, ref. 7).

potential in the liquid product that lends this class of ionic liquids a special tunability —to which more attention will be given in the last section of this article. The NTf_2 anion mentioned in the previous section serve equally well to lower the cohesion, hence also the fluidity, of these liquids. But the cohesion can also be manipulated by tuning the proton transfer energy, with the result that it is possible for protic ionic liquids, according to eqn (1), to become more conductive than the aprotic cases. Indeed, by taking advantage of these features, some of the most conductive liquids ever known, have been obtained.

3. Inorganic ionic liquids. These may be obtained, in both aprotic and protic forms, by taking advantage of the same packing problems that lead to low-melting ILs of the organic cation type. There may be fewer of them, but there are aprotic examples like lithium chlorate (melting point 115 °C), and its glassforming eutectic with lithium perchlorate, and protic examples like hydrazinium nitrate, $T_m = 80$ °C, not to mention low-melting mixtures of ammonium salts, and finally the largely unexplored cases of salts with inorganic molecular cations, such as PBr_3Cl^+, SCl_3^+, $ClSO_2NH_3^+$ *etc.*, with appropriate weak base anions.

4. Solvate (chelate) ionic liquids. These form a largely unstudied class of ILs that needs to be recognized because the class includes cases of multivalent cation salts that would not ordinarily be able to satisfy the criterion of $T_m < 100$ °C. The first recognized members of this class were molten salt hydrates, like $Ca(NO_3)_2 \cdot 4H_2O$, whose mixtures with alkali metal salts were found to be almost ideal mixtures, most with liquidus temperatures well below ambient.[14] These were hailed as a "new class of molten salt mixtures", but there has been some question about the lifetime of the water molecules in the cation coordination shell. This should be long with respect to the diffusion time scale for the "ionic liquids" classification to be unambiguous. Recently the Watanabe laboratory has described new cases where long lifetime is guaranteed because the ligating groups all belong to the same molecule. Thus instead