

Magnetic resonance spectroscopy in ionic liquids

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Contents

1. Introduction	64
1.1. Ionic liquids	64
1.2. The early years: chloroaluminate melts	64
1.3. “Second generation” ionic liquids	65
2. Binary ionic liquid systems	65
2.1. Speciation and equilibria	65
2.1.1. Aluminum speciation	68
2.1.2. Proton speciation	70
2.1.3. Oxygen speciation	72
2.1.4. Dual spin probe investigations	73
2.2. Physicochemical properties	73
2.3. Binary melts as solvents	75
3. Second generation ionic liquids	75
3.1. In molecular solvents	75
3.2. In pure form	77
3.3. Gas solubility and composition	80
3.4. Ionic liquids as solvents	81
4. Special topics	85
4.1. Chiral ionic liquids	85
4.2. Solvent reactivity	85
4.3. MAS techniques	86

Abbreviations: ARING, acoustic ringing (cancellation pulse sequence); bmim, 1-butyl-3-methylimidazolium; bmmim, 1-butyl-2,3-dimethylimidazolium; bmpy, 1-butyl-4-methylpyridinium; bpy, *N*-butylpyridinium; CAT-1, 4-trimethylammonium-2,2,6,6-tetramethyl-piperidine-1-oxyl iodide; CIDEP, chemically induced dynamic electron polarization; COSY, correlation spectroscopy; Cp, cyclopentadienyl; CP, cross polarization; DCM, dichloromethane; DQF, double quantum filtering; DMSO, dimethylsulfoxide; DSP, dual spin probe; emim, 1-ethyl-3-methylimidazolium; FAP, tris(perfluoroalkyl)trifluorophosphate; FWHM, full-width at half-maximum; HDPM, α -hydroxydiphenylmethyl; HMQC, heteronuclear multi quantum correlation; LED, longitudinal Eddy current delay; mppyr, *N*-methyl-*N*-pentylpyrrolidinium; mpy, *N*-methylpyridinium; NOE, nuclear Overhauser effect; NOESY, nuclear Overhauser enhancement spectroscopy; omim, 1-methyl-3-octylimidazolium; P_{14,6,6,6}, trihexyltetradecylphosphonium; POM, polyoxymethylene; PEEK, polyether ether ketone; PGSE, pulsed gradient spin echo; QCC, quadrupole coupling constant; ROESY, rotating frame Overhauser effect spectroscopy; scCO₂, supercritical carbon dioxide; SP, single pulse excitation; STE, stimulated echo; TEMPAMINE, 4-amino-2,2,6,6-tetramethyl-piperidine-1-oxyl; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl; TEMPOL, 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl; Tf₂N, bis(trifluoromethylsulfonyl)amide; TFO, triflate; TOCSY, total correlation spectroscopy; VT, variable temperature

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5. EPR spectroscopy in ionic liquids	87
6. Conclusions	88
Acknowledgement	88
References	88

1. Introduction

Ionic liquids (ILs) have gained tremendous attention in the last 15 years [1–16]. They are – among other uses – solvents and are frequently fitted with attributes like “modern”, “green”, “designable”, “non-volatile”, “non-coordinating” etc., although it is increasingly recognized that none of these labels should be used lightly.

Nonetheless, many chemical reactions have been attempted and successfully performed in ionic liquid media and oftentimes these systems show interesting and peculiar features [4,6–8,10–12,14–16]. Yet, considerable work in IL chemistry is still based on trial-and-error rather than fundamental understanding and rational design. Not enough is known to date about properties and structure of these new materials in the liquid phase nor are all observed differences in reaction outcomes as compared to “conventional” solvents explained satisfactorily.

To that end, suitable *in situ* methods that allow for thorough investigations are paramount. NMR spectroscopy is one obvious choice in this respect. In cases where radicals are involved, even more obviously, EPR spectroscopy is the method of choice. This review covers the chemical literature on NMR and EPR spectroscopy in the context of ionic liquids from the early eighties up to September 2006. The intent is to give the reader a comprehensive overview on magnetic resonance spectroscopy *on* and especially *in* these media. Works dealing only with the spectroscopic characterization of ionic liquids in molecular solvents are deliberately omitted.

1.1. Ionic liquids

An ionic liquid is – by definition – a material that (a) solely consists of ions and (b) has a low-melting point. A common notion defines “low” as “below 100 °C” [15], which is, of course, arbitrary. Hence, many people prefer to define “low” as “at room or reaction temperature”. Certainly, “low” is an approximate term, but in comparison to what is inferred from the preceding term “molten salt” (which is often equated with inorganic, high-melting and corrosive), this is used to demonstrate the usefulness of ionic liquids as solvents for chemistry.

Ionic liquids, when used as solvents for chemical reactions frequently induce different reactivities and selectivities when compared to conventional solvents. Ionicity leads to a relatively high polarity, yet ILs are not “super-polar”. Typical polarities fall in the range between acetonitrile and methanol; water is still more polar than most ILs [17]. To rationalize the differences between ILs and molecular solvents, it is important to understand the

(supra) molecular structure of the ionic liquid phase and possible equilibria within that phase.

A thorough overview of ionic liquids and their use in chemistry is beyond the scope of this review and may be found in numerous review articles [1–16]. In the following, only a brief introduction into the field will be given, reiterating the basic concepts needed to supplement the spectroscopic studies and their results presented in the main part.

1.2. The early years: chloroaluminate melts

Ionic liquids are no invention of recent years but have been around for quite some time, being referred to as “molten salts”. Their prime application was as electrolytes for electrochemistry [1,2,9]. In the mid-eighties, the term “ionic liquid” was popularized and used to denote a molten salt that could be used as solvent for *chemical* applications. The predominant structural motif at that time was that of mixed organic cation–chloroaluminate anion substances. A thorough review of this timespan is given by Welton [16].

Chloroaluminate ILs comprise “onium” chlorides combined with variable amounts of AlCl_3 (other metal halides were used as well). If mixed stoichiometrically, ILs of the [onium] AlCl_4 type are obtained. Disparate amounts (sub- or superstoichiometric) lead to anion mixtures. In the substoichiometric regime, the IL anion exhibits an equilibrium between AlCl_4^- and Cl^- . With superstoichiometric amounts of AlCl_3 , more involved mixtures of AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$ and higher aggregates emanate. Substoichiometric chloroaluminates are basic (Cl^-), while the superstoichiometric ones are acidic (AlCl_4^-) and its higher homologues being Lewis acids). Up to 1987, these melts were considered aprotic, yet all these chloroaluminates are extremely hygroscopic, hence traces of water are always present, making these mixed salts partially protic. Thus, the stoichiometry of the salt can have a substantial influence on a given chemical reaction. This peculiarity, together with intolerance towards air and moisture at the

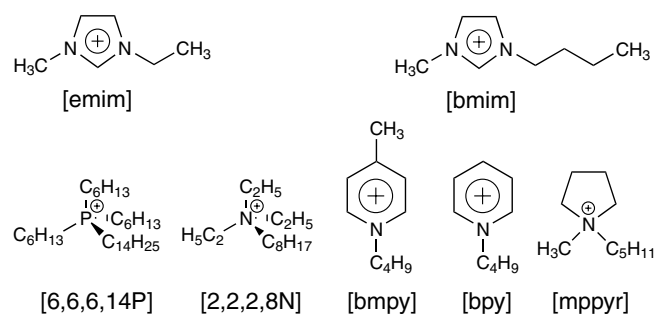


Fig. 1. Cations typically used for modern ionic liquids.

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