



Abstract Listing

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416537: Significance of cations in ionic liquids chemistry

IEC 0 [416537]: Significance of cations in ionic liquids chemistry

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ACCEPTED

Topic Selection: *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Ionic Liquid Systems*

Invited: *Y*

Preferred Presentation Format: *Oral*

Consider for Sci-Mix: *N*

Conforms to Bylaw 6: *Y*

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Abstract

There is a tendency to classify ionic liquids either as individual solvents (LiCl-KCl vs. NaCl-KCl, NaNO₃-KNO₃ vs. LiNO₃-KNO₃) or in terms of the anions. In fact, a compromise is appropriate. We shall point out how the cation choice influences the chemistry, including the electrochemistry, of an anion in an ionic liquid. Some examples follow. The effect of the cation on the structure of liquid alkali halides is exemplified by the coordination chemistry of dissolved Ni(II) as well as by diffraction studies. Raman spectroscopy demonstrates the cation influence on the fundamental equilibrium $2\text{AlCl}_4^- \rightleftharpoons \text{Cl}^- + \text{Al}_2\text{Cl}_7^-$ in alkali chloroaluminates. When the electrochemical reduction of NO₃⁻ in alkali nitrates is examined, we observe product! dependence that can be traced back to metal + oxygen reactions. Regarding the Lewis acidity of room temperature ionic liquids, it has been shown that the cracking of alkanes and the dissolution of heavy oil are influenced by the cation present with a given haloaluminate.

417133: Liquid ionic phosphates (LIPs): Syntheses and purifications

IEC 0 [417133]: Liquid ionic phosphates (LIPs): Syntheses and purifications

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Invited: *Y*

Comments to Organizer: *Immediately preceding our other submitted paper for this symposium (R. Engel last author)*

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Abstract

We herein report on two methods for the preparation of a new series of non-aqueous ionic liquids (NAILs). This new series of species incorporates polyammonium cations with phosphate anions. These liquid ionic phosphates (LIPs) are easily prepared from the corresponding halide salts, the syntheses of which have been previously reported. The first approach involves a modification of the previously described method for the preparation of NAILs using hexafluorophosphoric acid, incorporating as the anionic portion hexafluorophosphate anion. After precipitation of the water insoluble hexafluorophosphate salt from the reaction medium, removal of the remaining water yields the liquid ionic phosphate. Alternatively, LIPs can be prepared by two-phase anion exchange without the use of hexafluorophosphoric acid. Purification of all NAILs is considered, along with the full (H-1, C-13, P-31) NMR spectra for each species. While most efforts have focused on the polycationic species, corresponding preparation for NAILs based on simple pyridinium and imidazolium cations are discussed.

419149: New ionic liquids: Alkyl-substituted pyrylium salts and their conversion into pyridinium salts

IEC 0 [419149]: New ionic liquids: Alkyl-substituted pyrylium salts and their conversion into pyridinium salts

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Abstract

Diacylation of isobutene or its precursor (tert-butyl alcohol) with carboxylic anhydrides in the

presence of strong acids (hexafluorophosphoric, tetrafluoroboric, trifluoromethanesulfonic acid, etc.) affords 2,4,6-trisubstituted pyrylium salts with linear alkyl substituents in 2 and 6 positions. Their reaction with primary amines yields 1,2,4,6-tetrasubstituted pyridinium salts. Thus many new ionic liquids or low-melting salts were prepared. The melting points decrease with increasing length of the 2,6- and 1-alkyl groups; they also decrease in the following order of the anions for one and the same cation: $\text{PF}_6 > \text{BF}_4 > \text{CF}_3\text{SO}_3$. Anhydrous pyrylium salts melt at higher temperature than their crystallohydrates. Pyrylium tetrachloroferrates (2,4,6-trimethyl- or 2,3,4,6-tetramethyl-substituted) become liquids at room temperature on addition of aromatic hydrocarbons (e.g. toluene) or haloalkanes (e.g. chloroform). Addition of anhydrous aluminum chloride to molten pyrylium chloroferrates raises the melting point of the mixture.

419338: Ionic liquids in perspective: The past with an eye toward the industrial future

IEC 0 [419338]: Ionic liquids in perspective: The past with an eye toward the industrial future

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Abstract

Ionic liquids are now considered a special subset of molten salts, generally having 100 C in their liquidus range. Molten salts have a long and important history in industrial chemistry, but ionic liquids have found industrial applications somewhat more recently. The "modern" history of ionic liquids started with the development of aluminum chloride-based salts for electroplating in 1948. Since then the considerable basic research efforts have shown that ionic liquids may be used for batteries, organic and inorganic synthesis, spectroscopy, extractions, and alloy electrodepositions. The most commonly used type of cation in ionic liquids is the N,N'-dialkylimidazolium ion. The reason for the popularity of this slightly unusual cation is partly scientific and partly historic. The 21-year story of the development and uses of the imidazolium-based ionic liquids is an interesting example of multidisciplinary and multinational collaboration and competition.

423065: Highly acidic, non-chloroaluminate ionic liquids

IEC 0 [423065]: Highly acidic, non-chloroaluminate ionic liquids

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Abstract

In general, superacidic ionic liquids may be interesting, non-volatile replacements for commonly used superacids containing HF. However, the known superacidic systems based on chloroaluminate ions have some limitations. They are extremely oxophilic, thus forming adducts with C-O functionalities and reacting with traces of water to form HCl and Al-oxides. Our strategy is to use ionic liquids with anions of very low basicity. These media serve as suitable solvent for mineral acids such as sulfuric acid. For this purpose we developed new ionic liquids e.g. with the $[\text{B}(\text{HSO}_4)_4]$ anion. These melts are cheaply obtained by mixing [cation] HSO_4 , SO_3 and $\text{B}(\text{OH})_3$ in the right stoichiometry. Our results in the alkylation of benzene indicate that mixtures of sulfuric acid and e.g. $[\text{B}(\text{HSO}_4)_4]$ ionic liquid show higher catalytic activity than neat sulfuric. This behavior is explained by the weaker solvation of protons in the $[\text{B}(\text{HSO}_4)_4]$ ionic liquid in comparison to neat sulphuric acid.

438822: Working Salts. Syntheses and uses of ionic liquids containing functionalized ions

IEC 0 [438822]: Working Salts. Syntheses and uses of ionic liquids containing functionalized ions

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Abstract

We have prepared a number of ionic liquids containing cations and anions with appended functional groups. Water immiscible ionic liquids incorporating urea and thiourea groups are useful in the extraction of metal cations from aqueous phases. Others, with appended amine groups, have been shown to react with carbon dioxide and hydrogen sulfide, making them potentially useful in gas

scrubbing applications. We will discuss the synthesis and use of these and other functional ionic liquids. We will also report recent work on the absorption of ionic liquids by expandable clays. The absorption of ILs by montmorillonite is quite facile, and results in materials that may be regarded as supported IL phases. The synthesis and characterization of these materials will be presented, and some potential applications discussed. We will also point out the environmental implications of these interactions as they pertain to inadvertent industrial discharge of ionic liquids into soils.

445117: Intermission**0 [445117]: Intermission****ACCEPTED**

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445118: Discussion**0 [445118]: Discussion****ACCEPTED**

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