



Abstract Listing

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417134: Polycationic NAILs: Isolation of two types from hexafluorophosphoric acid reaction with polycationic halides

IEC 62 [417134]: Polycationic NAILs: Isolation of two types from hexafluorophosphoric acid reaction with polycationic halides

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ACCEPTED

Topic Selection: General Poster Session: Green (or Greener) Applications of Ionic Liquids

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Abstract

A series of polyammonium salts bearing phosphate or hexafluorophosphate anions has been prepared. These have both been isolated from the reaction of the previously synthesized halide salts with hexafluorophosphoric acid in aqueous medium. The resultant precipitate provides a mixture of the two types of salts, while the pure phosphate salt can be isolated from the supernatant by evaporation. NMR spectra (H-1, C-13, P-31) are used to determine the purity of these new liquid ionic phosphate salts (LIPs). Purification of the hexafluorophosphate salts is accomplished by repeated washings to remove the water-soluble phosphate salt impurity. These hexafluorophosphate salts as well have been fully characterized. These latter non-aqueous ionic "liquids" (NAILs) are solids of higher melting point than the previously described hexafluorophosphate NAILs involving monocationic pyridinium or imidazolium cations.

417199: Electrochemical and spectroscopic characteristics of polycationic liquid ionic phosphates

IEC 60 [417199]: Electrochemical and spectroscopic characteristics of polycationic liquid ionic phosphates

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Abstract

A series of polyammonium liquid ionic phosphates (LIPs) have been investigated for their electrochemical and spectroscopic properties. In particular, specific conductivities have been measured for a series of LIPs; specific conductivity values of 10-20 times greater than that for a standard aqueous KCl solution were observed. Electrochemical windows have been measured for these species by cyclic voltammetry using silver/silver phosphate and platinum electrodes. In addition, UV/Vis and fluorescence spectra have been measured for these species in aqueous solution. Further, diffusion coefficients for the species have been measured using pulsed gradient spin-echo NMR spectrometry.

417201: Polycationic salts: New anions with "strings" and "rings"**IEC 63 [417201]: Polycationic salts: New anions with "strings" and "rings"**

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Abstract

Prior work of our laboratory has been directed toward the synthesis and investigation of a variety of polycationic salts, both polyammonium and polyphosphonium species. Included in these prior efforts has been the preparation and characterization of a series of such polycations associated with phosphate and hexafluorophosphate anions. In the current work we are concerned with the preparation of salts of these same polycations associated with other types of anions, with a direction toward uncovering additional room temperature non-aqueous ionic liquid species (NAILS), as well as salts exhibiting minimum solubility in aqueous medium. In particular, nitrate, phosphate monoester dianion, and phosphate diester monoanion species have been used. We report on the preparation and characteristics of these species.

419017: Structure-property relationships in hexafluorophosphate-containing room-temperature ionic liquids

IEC 65 [419017]: Structure-property relationships in hexafluorophosphate-containing room-temperature ionic liquids

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Abstract

Room-temperature ionic liquids (RTILs) are attracting ever-increasing attention in many areas of analytical and organic chemistry. However, only a limited number of investigations have appeared which are directed toward understanding the nature of these novel solvents and the rational design of RTILs with required properties. Due to the low cost of starting materials, ease of preparation and handling, and a wide range of applications, hexafluorophosphate-containing imidazolium-based RTILs present an attractive system for studying structure-property relationships. Together with improved syntheses of precursor 1,3-disubstituted imidazolium bromides and the 1,3-disubstituted imidazolium hexafluorophosphates themselves, the effect of the structural variations within 1,3-disubstituted imidazolium hexafluorophosphates on their physico-chemical properties (e.g., phase transition temperatures, densities, viscosities, surface tension, etc.) will be described.

419517: Gas solubility and the effect on reactions in ionic liquids**IEC 56 [419517]: Gas solubility and the effect on reactions in ionic liquids**

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Abstract

Gas liquid reactions carried out in ionic liquids are not new and many have been reported in the literature with varying success. These include hydrogenations, oxygenations, carbonylations, etc. Of critical importance to the success of such reactions is the solubility of gases within the bulk reacting phase. Ideally, one would prefer high gas solubility leading to reduced reactor pressures, etc.

However, in situations of low gas solubility, certain engineering measures can be utilised to overcome these problems. The following paper reports a number of gas solubilities in commonly used ionic liquids and relates this data to the design of gas/liquid reactors.

419805: Potential application of ionic liquids for olefin oligomerization

IEC 48 [419805]: Potential application of ionic liquids for olefin oligomerization

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Abstract

Ionic liquids are emerging as an exciting alternative solvent technology with numerous promising green industrial applications. They provide a unique solvent environment, quite unlike any of the generally used traditional systems. This new technology field provides ample opportunities for novel ways of synthesising well-known compounds more efficiently, as well as for the synthesis of novel compounds. The poster presentation will discuss the use of room temperature ionic liquids as part of biphasic catalysis systems for industrial application areas, focusing on olefin oligomerisation processes.

The following aspects will be addressed: * General potential and advantages of using ionic liquid technology in industrial relevant processes. * The use of ionic liquids as oligomerisation catalysts. * Ionic liquids as an alternative solvent for chromium catalysed ethylene and olefin oligomerisation processes. * An assessment of the possibilities for the utilisation of ionic liquids as part of metallocene catalysed oligomerisation processes. * Future research work planned.

420620: Photoinduced energy transfer and hydrogen abstraction reactions in ionic liquids

IEC 57 [420620]: Photoinduced energy transfer and hydrogen abstraction reactions in ionic liquids

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Abstract

Room temperature ionic liquids are finding increasing interest as solvents in a range of applications, notably organic synthesis, two-phase catalysis, and electrochemistry. However, virtually nothing is known about their behaviour as solvents for photochemical reactions. We have carried out laser flash photolysis studies of important photoinduced processes in ionic liquids, notably the energy transfer reaction between triplet excited state benzophenone and naphthalene. The rate and thermodynamic parameters were determined in various ionic liquids and compared to those obtained in conventional solvents. We have also studied the abstraction of hydrogen by photoexcited aromatic carbonyl compounds in ionic liquids. The $3(n, \pi^*)$ state of these compounds efficiently abstracts a hydrogen atom from H-donor solvents, such as alcohols and hydrocarbons. This process has been studied in a range of imidazolium based ionic liquids, and the effect on the reaction of differing alkyl substituents on the heterocyclic ring will be discussed in this paper.

420626: Ionic liquids: Clean solvents for organic synthesis

IEC 55 [420626]: Ionic liquids: Clean solvents for organic synthesis

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Abstract

Ionic liquids have been employed as solvents for an ever-increasing range of organic and biphasic catalysis reactions. We have taken advantage of their unique properties to address two important synthetic processes. The first system is the allylation of carbonyl compounds to generate homoallylic alcohols. When carried out in ionic liquids using tetraallyl tin as the allylating agent, excellent yields are obtained for aldehydes at room temperature, while ketones require elevated temperatures. The use of ionic liquids as reaction solvents for this reaction allows easy separation of the organic products via solvent extraction, while the toxic tin-containing residues are retained within the ionic liquid. Recycling of the ionic liquid for multiple reactions is also very simple, requiring only washing with aqueous base to remove the tin residues. Also under investigation is transition metal catalysed hydrosilylation of alkenes and carbonyl compounds. We have looked at the reactions using a range of silanes along with catalysts such as H_2PtCl_6 and $RhCl(PPh_3)_3$. The potential for recycling the catalyst will also be discussed.

425566: Comparative study of the chemical and physical properties of hydrophobic versus hydrophilic ionic liquids**IEC 49 [425566]: Comparative study of the chemical and physical properties of hydrophobic versus hydrophilic ionic liquids**

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Abstract

Ionic Liquids (IL) have attracted a lot of attention, particularly as solvent alternatives due to their low volatilities, unique chemistries, and, significantly, the ability to fine-tune their solvent properties via manipulation of the component ions. IL are composed of cations and anions such that the physical properties of the resulting liquid are affected by small changes in the type or structure of both the cation or anion. This presentation will compare physical property data we have obtained for IL based on the 1-alkyl-3-methylimidazolium cation with various anions which probe both hydrophilic and hydrophobic IL.

429193: Plutonium chemistry in room temperature ionic liquids**IEC 59 [429193]: Plutonium chemistry in room temperature ionic liquids**

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Abstract

Room temperature ionic liquids (RTIL) are an important class of solvents whose unique set of chemical and physical properties hold the promise of making revolutionary changes in many traditional chemical processes. We have previously reported on the redox behavior of uranyl chloride in room temperature acidic 1-ethyl-3-methyl imidazolium chloride by electrochemical and spectroscopic techniques. Spectroscopic and electrochemical results on plutonium in the +3, +4 and +6 oxidation

states will be presented. We have demonstrated that a basic EMIC/ AlCl_3 solution of PuCl_3 displays one reversible oxidation and an irreversible reduction. The reversible wave has been confirmed to be associated with the Pu(III)/Pu(IV) redox couple by comparison with the CV of an authentic sample of Cs_2PuCl_6 . The irreversible reduction wave is believed to come from the reduction of a plutonium oxide contaminant. We will also present data relating to criticality concerns with respect to actinide processing in RTIL systems.

434542: Highly acidic ionic liquids for carbonylation of aromatic compounds

IEC 61 [434542]: Highly acidic ionic liquids for carbonylation of aromatic compounds

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Abstract

The introduction of cleaner technologies has become a major concern throughout industry today. As a result, the re-evaluation and re-thinking of old existing chemical processes that have proved otherwise satisfactory have become high priority. The potential of room temperature ionic liquids to be used as effective solvents and catalysts for clean synthesis make them especially suitable for use in aromatic transformation reactions, which is often accompanied by large effluent generation. A good example is the acid catalyzed carbonylation of an aromatic compound to produce the corresponding aromatic aldehyde using carbon monoxide. Since an acidic ionic liquid can be either Lewis or Bronsted in nature, ionic liquids are potential catalysts for aromatic carbonylation reactions. Currently, the carbonylation of aromatic compounds represents an attractive opportunity to produce downstream products of higher value. The results that will be presented summarize a study on the use of highly acidic ionic liquids in the carbonylation of aromatic compounds.

438299: Organostannanes and ionic liquids: Toward green chemistry

IEC 64 [438299]: Organostannanes and ionic liquids: Toward green chemistry

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Abstract

Organostannanes are widely used in synthetic organic chemistry; however, they are thought of as environmentally unfriendly, and present numerous problems in product purification.

During the course of this paper we highlight some of our recent work. In particular the use of organostannanes in the development of an efficient and environmentally friendly protocol. This protocol allows reactions to be conducted in environmentally benign solvents, water and ionic liquids, with high atom efficiency and high yields.

The reactions are highly atom efficient, with only the tin remaining unutilised, and this can be recovered as "inorganic tin".

438328: Supported ionic liquid membranes and facilitated ionic liquid membranes**IEC 54 [438328]: Supported ionic liquid membranes and facilitated ionic liquid membranes**

Paul Scovazzo¹, Ann E. Visser², James H. Davis Jr.³, Robin D. Rogers², Carl Koval⁴, and Richard D. Noble¹. (1) Department of Chemical Engineering, University of Colorado, Campus Box 424, Boulder, CO 80309, scovazzo@colorado.edu, (2) Department of Chemistry and Center for Green Manufacturing, The University of Alabama, (3) Department of Chemistry, University of South Alabama, (4) Department of Chemistry and Biochemistry, University of Colorado

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Abstract

Supported Liquid Membranes (SLM's) use porous supports whose pores are impregnated with a solvent. In SLM's, solute molecules dissolve into the membrane at the feed/membrane interface. The dissolved species diffuse through the membrane and desorb at the opposite membrane surface. The addition of a third mobile chemical or carrier to the solvent that can reversibly bind to the dissolved species enhances the selectivity of the membrane (facilitated transport). The disadvantages of SLM's are the loss of solvent via volatilization and the loading limits (solubility) on complexing agents in the solvent that limits the obtainable flux rate. Unlike the solvents currently used in SLM's, Room

Temperature Ionic Liquid (RTIL) properties may be adjusted via chemical alteration of the ions to produce “designer solvents” for a specific membrane application. The potential exists for complexing agents to be one of the ions giving a mole fraction loading of a complexing agent in the solvent of one, much greater than the loadings in standard systems. Supported Ionic Liquid Membranes (SILM) also have an advantage over SLM's due to the RTIL's negligible loss through vaporization. Our initial research focus is on the CO₂ separation from N₂ using RTIL's with and without ionic and non-ionic doping compounds. We have proven the concept of SILM's. In addition, we are determining the basic principles for developing working Facilitated Ionic Liquid Membranes (FILM's). Our paper presents the proof-of-concept of SILM's, the basic principles of FILM development, and discusses future needs for continued development of SILM's and FILM's.

441020: Electrochemical and EXAFS investigations of uranium compounds in ionic liquids

IEC 58 [441020]: Electrochemical and EXAFS investigations of uranium compounds in ionic liquids

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Abstract

Considerable attention has been given to the use of room temperature ionic liquids (RTIL) systems as alternative solvents for both organic and inorganic chemistry. High temperature (> 600 K) molten salt solvent systems have been investigated for use in the nuclear industry. Substituting ionic liquid systems with lower melting points and operating temperatures for high temperature molten salts is a possible progression of technology. Many of the motivating advantages gained from the use of molten salts in reprocessing, might be maintained while gaining the benefits of operating at lower temperatures and with less corrosive materials. There is already a widespread interest in using ionic liquids in the nuclear industry. We report the preparation of a number of uranium compounds, including the dimeric dioxouranium(VI) nitrate oxalato compound [C₈H₁₅N₂]₂[{UO₂(NO₃)₂}(μ-C₂O₄)], in ionic liquid media. These compounds, many of which are electrochemically active, have been analysed using voltammetry, single crystal powder X-ray diffraction, and extended X-ray absorption fine structure spectroscopy.

441097: Characteristics of room temperature ionic liquids in various water/ethanol

solutions**IEC 50 [441097]: Characteristics of room temperature ionic liquids in various water/ethanol solutions**

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ACCEPTED

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Abstract

Room Temperature Ionic Liquids (RTIL) are gaining a great deal of attention due to their remarkable solvent properties; including negligible vapor pressure, air and water stability, and high thermal stability. Also, the ability to fine-tune these solvents makes them prime candidates as alternatives to VOCs in many chemical processes. The solubility of ethanol in the 1-butyl-3-methylimidazolium hexafluorophosphate is controlled by the mole fraction of water, with a biphasic system forming between both 0.5 to 0.9 mole fraction ethanol. Certain ethanol/water solution may be used to totally solubilize the RTIL. This presentation will discuss the physical characteristics of various RTIL with regards to changes in mole fraction of ethanol. This work is supported through a grant from the U.S. Environmental Protection Agency.

442608: Solubility of mono- and di-saccharides in ionic liquids**IEC 53 [442608]: Solubility of mono- and di-saccharides in ionic liquids**

Scott K. Spear¹, Grant A. Broker², Marc A. Klingshirn², Luc Moens³, Mary An Godshall⁴, Tere Pi Johnson⁵, and Robin D. Rogers⁶. (1) Center for Green Manufacturing, The University of Alabama, Box 870336, Tuscaloosa, AL 35487, Fax: 205-348-0823, sspear@bama.ua.edu, (2) Department of Chemistry, The University of Alabama, (3) Center of Chemistry for BioEnergy Systems, National Renewable Energy Laboratory, (4) Sugar Processing Research Institute, Inc, (5) Sugar Cane Growers Cooperative of Florida, (6) Department of Chemistry and Center for Green Manufacturing, The University of Alabama

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Abstract

Ionic liquids offer a new class of solvents with environmentally favorable characteristics that are just being explored within the realm of biological materials and biomolecules. Therefore, the need for fundamental physical measurements such as solubilities is necessary. One class of biomolecules that we have chosen to study within ionic liquids is carbohydrates. This work presents our results to date measuring solubilities of several key mono- and di-saccharides in ionic liquids.

442636: Free energy relationships and solvatochromic properties of aqueous solvent systems based on poly(ethylene) glycol**IEC 51 [442636]: Free energy relationships and solvatochromic properties of aqueous solvent systems based on poly(ethylene) glycol**

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Abstract

Linear Free Energy Relationships and Solvatochromic parameters have provided a convenient means of characterizing the properties of molecular solvents because of their ability to encapsulate such important practical properties as solubilities, partition constants and reaction rates. We have attempted to characterize the solute distribution and solvatochromic properties of a series of aqueous biphasic systems, which may find application as alternatives to organic solvent systems, using these two approaches. The first is based on the solvatochromic shift in the wavelength of absorption of various dyes, including 4-nitroanisole, Reichardt's betaine and 4-nitrophenol when dissolved in the aqueous polymeric solutions. The second involves determination and correlation of the distribution of selected solutes between the co-existing phases of aqueous biphasic systems. The results of these studies will be reported and the solvent properties will be discussed in terms of potential applications of aqueous biphasic extraction technology.

442842: Solubilization and derivatization of chitin in room temperature ionic liquids**IEC 52 [442842]: Solubilization and derivatization of chitin in room temperature ionic liquids**

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Abstract

Research priorities laid out in the Vision 2020 Technology Roadmap for Renewable Resources include the use of biorenewables. In the shellfish industry more than 85% of the waste produced is in the form of insoluble shells, whose major component is chitin. Ionic liquids have been shown to be excellent replacements for traditional organic solvents in liquid/liquid extractions. Recently we have seen that RTILs can also act as novel solvents in the dissolution of chitin, the major component in the shells. This presentation will focus on the methods of dissolving refined and processed chitin and some derivatization of the chitin, e.g., chitosan a water-soluble form of chitin.
