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Stability of Ionic Liquids in Air and Water

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Abstract

Ionic liquids are liquids that only contain cations and anions and, by definition, must have a melting point of 100 1C or lower. Originating from electrochemistry in AlCl3-based liquids, tremendous progress has been made in the last ten years to synthesise ionic liquids that can be handled under ambient conditions, with approximately 300 ionic liquids now commercially available. While organic and technical chemistry remain of primary interest, various aspects of physical chemistry in ionic liquids are now being discussed in the literature. We provide a brief overview of physicochemical aspects of ionic liquids in this review article, including physical properties of ionic liquids, nanoparticles, nanotubes, batteries, spectroscopy, thermodynamics, and catalysis of/in ionic liquids.The emphasis is on air and water stable ionic liquids, which are expected to dominate various fields of chemistry in the future.

Introduction

Walden published the first report of a room temperature molten salt in 1914, which began the early history of ionic liquids. [1] He described the physical properties of ethyl-ammonium nitrate, $[C_2H_5NH_3]$ NO_3, which is formed by the reaction of ethylamine with concentrated nitric acid and has a melting point of 121^0C. Hurley and Weir [2] then claimed that by mixing and warming 1-ethylpyridinium chloride with aluminium chloride, they could create a room temperature ionic liquid. Osteryoung et al. [3,4] and Hussey et al. [5-7] conducted extensive research on organic chloride-aluminum chloride ambient temperature ionic liquids in the 1970s and 1980s, and Hussey wrote the first major review of room temperature ionic liquids. [8] The ionic liquids based on $AlCl_3$ can be regarded as the first generation of ionic liquids.

The hygroscopic nature of $AlCl_3$-based ionic liquids has slowed their adoption in many applications because they must be prepared and handled in an inert gas atmosphere. Thus, the synthesis of air and water stable ionic liquids, known as the second generation of ionic liquids, sparked renewed interest in the use of ionic liquids in a variety of fields. Wilkes and Zaworotko [9] reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cation with tetra-fluoroborate or hexa-fluorophosphate anions in 1992. These ionic liquids, unlike chloroaluminate ionic liquids, could be prepared and safely stored outside of an inert atmosphere.These ionic liquids are generally water

insensitive; however, prolonged exposure to moisture can cause changes in their physical and chemical properties. Using in situ scanning tunnelling microscopy, we discovered that the undried ionic liquid [BMIm] PF_6 attacks the gold substrate, and its aggressiveness increases as the water content increases. This is due to the formation of HF as a result of ionic liquid decomposition in the presence of water. Ionic liquids based on more hydrophobic anions, such as tri-fluoromethanesulfonate ($CF_3SO_3^-$), bis-(trifluoromethanesulfonyl) imide [$(CF_3SO_2)_2N$], and tris-(trifluoromethanesulfonyl) methide [$(CF_3SO_2)_3C^-$], have been developed as a result. [10–12] These ionic liquids have gotten a lot of attention not only because of their low water reactivity, but also because of their large electrochemical windows. Typically, these ionic liquids can be well dried under vacuum with water contents below 1 ppm at temperatures ranging from 100 to 150^0C.

As can be seen, the average number of publications over the last decade has been around 40 papers per year, with about 1000 papers published in 2004 and about 1500 papers published in 2005. This reflects a general increase in interest in ionic liquids.

Aside from the pioneers in the field of ionic liquids, such as Osteryoung, Wilkes, Hussey, and Seddon, there are several scientists, such as Rogers, Welton, Wasserscheid, MacFarlane, Ohno, Endres, Davis, Jr, Abbott, and others, who entered this field and had a significant impact in introducing ionic liquids in many applications.

Rogers is a well-known author in the field of ionic liquids. He is particularly interested in the synthesis and characterization of environmentally friendly ionic liquids for use as green solvents. He measured and published data on the physicochemical properties of many ionic liquids in order to provide data to begin evaluating the use of ionic liquids in a variety of processes. He also works on the development of new cellulose materials using ionic liquids.

Welton has authored numerous papers on the use of ionic liquids as solvents in synthesis and catalysis. He studies how ionic liquids interact with solute species to affect their reactivity, and he works to replace environmentally hazardous solvents with less harmful alternatives. He also wrote one of the most cited papers [13], which was cited 1719 times as of November 2005.

Wasserscheid is a member of the ionic liquid community who specialises in the preparation and characterization of ionic liquids for use in biphasic catalysis. He could, for example, demonstrate that using hexafluorophosphate ionic liquids allows for selective, biphasic oligomerization of ethylene to 1-olefins. He co-edited an important book, Ionic Liquids in Synthesis, with Welton, that discusses the synthesis and physicochemical properties of ionic liquids, as well as their applications in catalysis, polymerization, and organic and inorganic synthesis. [14]

MacFarlane is working on the synthesis of new air and water stable ionic liquids with the goal of using them as indicators for sensing and displaying an environmental parameter such as humidity. The colour change of the ionic liquids where they are synthesised with either a coloured cation or anion controls this process, so the ionic liquids themselves are sensors. He has also published numerous papers on the use of ionic liquids in electropolymerization and batteries.

Ohno's research focuses on the synthesis of polymerizable ionic liquids and their polymerization to create a new class of ion conductive polymers. For example, by combining nitrite rubber (poly(acrylonitrile-cobutadiene) rubber) with the ionic liquid N-ethylimidazoliumbis(trifluoromethanesulfonyl)imide, he created polymer electrolytes with high ionic conductivity and good elasticity. He recently edited a book titled Electrochemical aspects of ionic liquids, which introduces some basic and advanced ionic liquid studies in the field of electrochemistry. [15]

For the first time, we were able to demonstrate that Ge, Si, Se, Ta, and Al can be electrodeposited in high quality in air and water stable ionic liquids. Many more elements and compounds can presumably be created electrochemically. Some recent nanoscale electrodeposition results in water and air stable ionic liquids will be presented.

Physical Properties of ILs

Conductivity

Ionic liquids have relatively high ionic conductivities when compared to organic solvent/electrolyte systems (up to B10 mS cm1). [16] Some systems can achieve a conductivity of 0.1 O1 cm1 at elevated temperatures, such as 200 1C. However, their conductivities at room temperature are typically lower than those of concentrated aqueous electrolytes. Ionic liquids are expected to have high conductivities due to the fact that they are made up entirely of ions. This is not the case because any solution's conductivity is determined not only by the number of charge carriers but also by their mobility. Ionic liquids' large constituent ions reduce ion mobility, resulting in lower conductivities.In addition, ion pair formation and/or ion aggregation reduce conductivity. Ionic liquid conductivity is inversely proportional to their viscosity. As a result, higher viscosity ionic liquids have lower conductivity. Temperature increases conductivity while decreasing viscosity.

Melting Point

Ionic liquids have been defined as having melting points below 100 1C and being liquid at room temperature. Cations and anions both contribute to ionic liquids' low melting points. The melting point decreases as anion size increases. [24] Melting points of 1-ethyl-3-methylimidazolium type ionic liquids with different anions, such as [BF4] and [Tf2N], for example, are 151^0C 25 and 31^0C,10, respectively. The melting points of ionic liquids are greatly influenced by the size and symmetry of cations. A melting point decrease is caused by large cations and increased asymmetric substitution. [26]

Viscosity

Ionic liquids are generally more viscous than common molecular solvents, with viscosities ranging from 10 mPa s to 500 mPa s at room temperature. At room temperature, the viscosities of some popular air and water stable ionic liquids are as follows: 312 mPa s for [BMIm]PF_6; [17] 154 mPa s for [BMIm]BF4; 18 52 mPa s for [BMIm]TF_2N; 10 85 mPa s for [BMP]TF2N. 12 Van der Waals forces and hydrogen bonding determine the viscosity of ionic liquids. Electrostatic forces may also be important. The lengthening of the alkyl chain in the cation causes an increase in viscosity. [10] The increased energy required for molecular motion is due to stronger van der Waals forces between cations. Furthermore, the ability of anions to form hydrogen bonds has a significant effect on viscosity. Because of hydrogen bonding, fluorinated anions such as BF4 and PF6 form viscous ionic liquids. [19] In general, as temperature rises, the viscosity of all ionic liquids decreases significantly (see, e.g., ref. 20).

Electro-synthesis of Stable ILs in Air and Water

In this section, we will discuss the use of some popular air and water stable ionic liquids in bulk electrodeposition of metals and semiconductors, such as ZnCl2/[EMIm] Cl, [EMIm] BF_4, [BMIm] BF_4, [BMIm] PF_6, [BMP] Tf_2N, [BMIm] Tf_2N, and choline chloride-MCl. Furthermore, we will discuss nanoscale processes at the electrode/ionic liquid interface as well as electro-polymerization. We concentrate solely on the novel air and water stable liquids because we believe they will be of significant interest in several aspects of electrochemistry.

Electrodeposition of Alloys and Metals

According to Katayama et al. [29], a room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF_4) can be used as an alternative electroplating bath for silver. The ionic liquid [EMIm]BF_4 outperforms chloroaluminate

systems because silver electrodeposition can be performed without the risk of aluminium codeposition. In ref. 30, silver was electrodeposited in the ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) and [BMIm]PF_6.Cd, [31] Cu [32], and Sb [33] can also be electrodeposited in a solution of 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIm]BF_4) and [EMIm]Cl. Sun et al. recently demonstrated the electrodeposition of compound semiconductors such as indium antimonide (InSb) [34] and cadmium telluride (CdTe) [35] in the Lewis basic 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid [BMIm]BF4. InSb is a III-V compound semiconductor, while CdTe is an II-VI semiconductor. Both are widely used in a variety of applications, including electronic devices and solar cells.

According to ref. [36], titanium can be electrodeposited in thin layers of about 5 nm in the ionic liquid 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [BMIm] Tf_2N at room temperature. The challenge in depositing micrometre thick solely metallic layers with all refractory metals is to avoid the formation of non-stoichiometric subhalides.Ionic liquids have been created by combining zinc chloride with pyridinium-, [37]dimethylethylphenyl-ammonium-, [38] 1-ethyl-3-methylimidazolium chloride [EMIm]Cl and 1-butyl-3-methylimidazolium chloride [BMIm]Cl. [39-41] These ionic liquids are simple to make and do not decompose when exposed to water and air. According to [42], the potential limits for a basic 1: 3 $ZnCl_2$-[EMIm]Cl ionic liquid correspond to cathodic reduction of [EMIm] and anodic oxidation of Cl, resulting in an electrochemical window of approximately 3.0 V.For acidic ionic liquids with a $ZnCl_2$-[EMIm]Cl molar ratio greater than 0.5:1, the negative potential limit is due to metallic zinc deposition, and the positive potential limit is due to chlorozincate complex oxidation. As a result, the electrodeposition of Zn and its alloys in Lewis acidic liquids is possible. Lewis acidic $ZnCl_2$-[EMIm]Cl (with a molar percentage of ZnCl2 greater than 33 mol%) has been demonstrated to be potentially useful for the electrodeposition of zinc and zinc-containing alloys. [43–45] Pt-Zn alloy, [46] iron and Zn-Fe alloy, [47] tin and Sn-Zn alloy, [48] cadmium and Cd-Zn alloy [49] can all be electrodeposited in Lewis acidic $ZnCl_2$-[EMIm]Cl ionic liquids, according to Huang and Sun.

Electrodeposition on Nanoscale

We began conducting in situ STM studies on electrochemical phase formation in ionic liquids for the first time nearly ten years ago. On the one hand, there was no knowledge of the local processes of phase formation in ionic liquids; on the other hand, these systems provide access to elements that are not available in aqueous solutions, such as Al, Ge, Si, Ta, and many others. We see a great opportunity for electrodeposition of nanostructures in ionic liquids, particularly in the rapidly growing field of nanotechnology, where semiconductor nanostructures will play an important role. The electrochemical processes and factors that influence deposition and structure stability must be understood on the nano-meter scale for this purpose.

Electro-synthesis of Conducting Polymer

Conducting polymers have sparked significant interest as new materials for the development of a wide range of electrochemical devices, including batteries, supercapacitors, sensors, electrochromic devices, electrochemical actuators, and light emitting diodes. [50] These polymers can be created through chemical or electrochemical polymerization. Some advantages of electrochemical synthesis include the generation of polymers in the doped state and the easy control of film thickness. Furthermore, electro polymerization is a simple and quick process.

Catalysis

Ionic liquids are now widely used in catalysis as catalysts or catalyst activators as well as solvents or reaction media. We give only a few examples of the use of some air and water

stable ionic liquids in catalysis because there are a number of excellent reviews134-137 on the application of ionic liquids in catalysis and bio-catalysis.

Conclusion

We attempted to provide an overview of the importance of ionic liquids in physical chemistry in this review article, and we summarised literature up to the end of 2005. Whereas ionic liquids were thought to be relatively new until around the year 2000, the situation has changed dramatically in the last three years. There were approximately 1500 peer-reviewed papers on ionic liquids in 2005. The continued interest in ionic liquids in various fields of chemistry will undoubtedly result in an increase in the number of papers published, stimulating further research. Ionic liquids are expected to become a mainstay in many fields of chemistry and physical chemistry in the near future.We are very interested in future developments in this field and look forward to reading many more papers about these fascinating liquids.

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