Highlight Review

Task-Specific Ionic Liquids

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(Received May 17, 2004; CL-048007)

Abstract

The covalent tethering of a functional group to one or both of the ions of an otherwise ordinary ionic liquid can imbue the resulting salt with a capacity to interact with dissolved substrates in specific ways. Called "task-specific" ionic liquids (TSIL), these low melting salts are finding an increasing number of applications in synthesis, separations, catalysis, and electrochemistry.

◆ Introduction

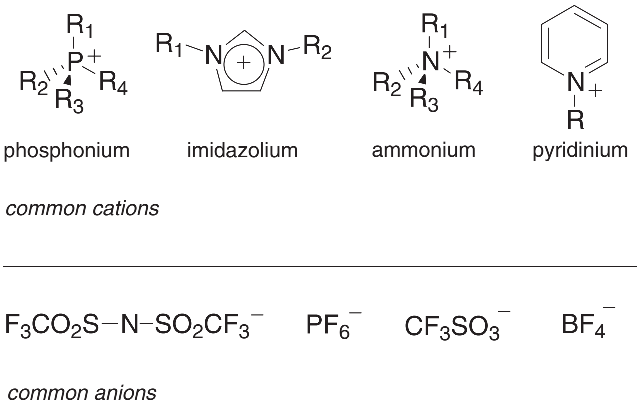
For almost a century, the study of molten salts was the near-exclusive domain of electrochemists.[1] However, since the early 1990s there has been a growing interest in expanding the sphere of use of certain molten salts —ionic liquids (IL)— to other applications as well.[1–4] Defined as salts which melt below 100 °C, and which in their molten form are composed solely of ions, ionic liquids constitute a remarkably promising class of technologically useful and fundamentally interesting materials.[1] Demonstrated or proposed applications of IL range from their use as non-volatile, non-flammable solvents to advanced heat transfer fluids and lubricants. All are applications which stand to benefit from a key attribute manifested by these unorthodox liquids: no measurable vapor pressure.[1–4]

It is probably fair to say that to most chemists the term "molten salt" conjures up images of crucibles containing red-hot lava. For common salts like NaCl the image is a valid one. The melting point of any salt is dictated by the electrostatic potential which exists between its cations and anions, and for salts such as NaCl this potential is very high. In turn, the melting points of salts are reflections of this electrostatic potential, specifically expressed as their lattice energy (Eq 1).

$$E = k\frac{Q_1 Q_2}{d} \qquad (1)$$

In Eq 1, k is the Madelung constant, Q_1 and Q_2 the charges on the ions, and d the interionic separation. With larger ions, d is effectively larger, resulting in a smaller lattice energy and lower melting point. And, while it is not immediately obvious from the form of the equation itself, mismatches in the sizes and shapes of the ions tend to impede efficient ion packing, also contributing to an effective increase in d. Consequently, salts of ions in which there is a significant ion size and/or shape mismatch are expected to exhibit significantly diminished lattice energies, with lower melting points as a result. Nevertheless, the global electrostatic potential still prevails, with every cation and anion in the sample attracted to the other. Together, these phenomena appear to account for the low melting points and non-measurable vapor pressures of ionic liquids.

The majority of ionic liquids research that has been done so far has made use of a small group of salts.[1,5] By in large these are quaternary ammonium, phosphonium, imidazolium, or pyridinium cations with large, charge-diffuse inorganic counterions (Figure 1). In these salts, the cation core has appended to it one or more organic groups. Typically, these groups are saturated hydrocarbon fragments. A number of reviews of the chemistry of these "conventional" ionic liquids are available, as is at least one textbook on IL technology.[1] It should also be noted that ionic liquids of these types are increasingly commercially available.[5]



$F_3CO_2S{-}N{-}SO_2CF_3^-$ PF_6^- $CF_3SO_3^-$ BF_4^-

Figure 1.

◆ The TSIL Concept

In one critical sense —vapor pressure— ionic liquids constitute "liquid solids." It is important to note that the use of solid supports for chemical functionality is a technology of enormous importance (e.g., solid acid catalysts, scavenging reagents for solution-phase synthesis, supports for solid-phase synthesis, etc.).[6] It is equally noteworthy that in many cases the key drivers for the use of solid reagents are their lack of vapor pressure or their phase heterogeneity, the latter facilitating product isolation. Still, solid reagents are fraught with drawbacks of their own, including heterogeneous kinetics and a susceptibility to ready deactivation.[6] Further, with many solid reagents a high proportion of the reagent mass and volume serves solely as scaffolding for

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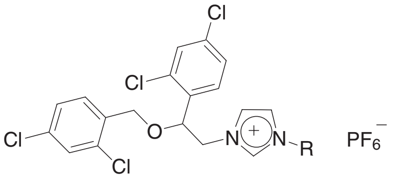
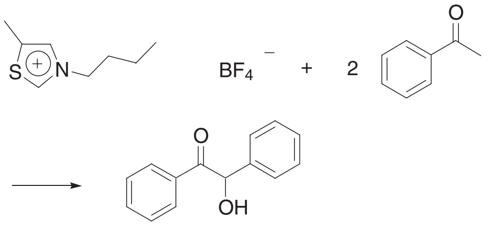
the chemical functionality. The latter tend to constitute significant engineering drawbacks. Consequently, a valuable middle ground would be found in chemically functional liquids that, like solids, have no vapor pressure and which are also readily separated from product.



R = Me, Et, n-Bu, $(CH_2)_2(CF_2)_5CF_3$;
No R group in the parent drug miconazole.

Figure 2.

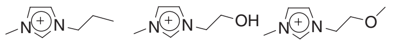
In 1998, we introduced several ionic liquids in which the cation was derived from the antifungal drug miconazole (Figure 2).[7] While the cations were imidazolium-type species, their size and complexity were outside the norm for cations which to that point were being used for IL formulation. As a result, we began to consider the possibilities that might exist for creating ionic liquids with unusual ions. Specifically, we wondered if it might be possible to build ions that not only serve as components of a solvent, but that manifest specific types of interactions with dissolved substrates. At least one type of ionic liquid was already well-known for its solvo-catalytic behavior, the azolium chloroaluminates (vide infra).[1]



Scheme 1.

In 1999, we demonstrated the concept of *designing* IL to interact with a solute in a specific fashion, showing that a thiazolium IL could function as solvent-catalyst for the benzoin condensation (Scheme 1).[8] We then outlined our concept in a brief review, introducing the term "task-specific ionic liquids" (TSIL) to describe IL which incorporate functional groups designed to impart to them particular properties or reactivities.[9] We subsequently disclosed additional preliminary results in various venues.[2–4,10] It is important to note that about this same time, other groups were also beginning to develop functionalized ions for use in IL, and several elements of that chemistry are presented in this review. We have included discussions of ionic liquids which contain functional groups even where they have not been specifically described by their inventors or users as TSIL.

There are several rationales for the incorporation of a functional group into an IL. First, the inclusion of the functional group will doubtless alter the solvent parameters of an IL relative to an analog bearing a simple hydrocarbon appendage. These parameters —dipolarity, H-bond acidity and basicity, polarizability, etc.— are the attributes which make any chemical a good or poor solvent for a given solute.[11] Interestingly, to our knowledge only one study has so far attempted to quantify the effect of functional groups on IL properties. In that case, Bartsch measured the polarity alcohol and ether functionalized imidazolium salts of $[(CF_3SO_2)_2N]^-$ using Reichardt's dye as a solvatochromic probe.[12] For those compounds, the observed values of $E_T(30)$ were 60.8 and 61.4, respectively. Juxtaposed against an $E_T(30)$ of 52.0 for 1-methyl-3-propylimidazolium bis(triflyl)-imide, an increased polarity arising from the inclusion of the functional group was proposed. Further, the authors showed that the apparent polarity difference manifested itself in a practical fashion, influencing the *endo*/*exo* ratio of Diels–Alder products formed between cyclopentadiene and methyl acrylate (Figure 3).



$E_T(30)$	52.0	60.8	61.4
endo/exo	4.3	6.1	5.7

all IL as $(CF_3SO_2)_2N^-$ salts

Figure 3.

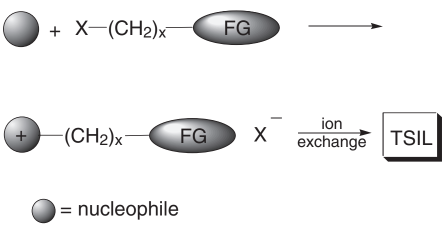
Still, as has been pointed out elsewhere, the data obtained from spectroscopic probes yields only a partial picture of a solvents' overall solvent parameters (Abraham parameters).[1] That being the case, further physical studies of functional group effects on IL properties is clearly merited.

A second rationale for the inclusion of a functional group in an IL is to imbue the salt with a capacity to covalently bind to or catalytically activate a dissolved substrate. This area of TSIL research has been the most active, and TSIL of this genre are now being used in both synthetic and separations applications. Significantly, it is in this application mode that parallels between TSIL and solid supported reagents are the most obvious. Several of these uses are discussed in greater detail below. Finally, Scammells, et al. have shown that the incorporation of certain functional groups (especially esters) increases the rate of breakdown of an IL in the environment, a factor of considerable practical importance.[13]

TSIL Synthesis and Characteristics

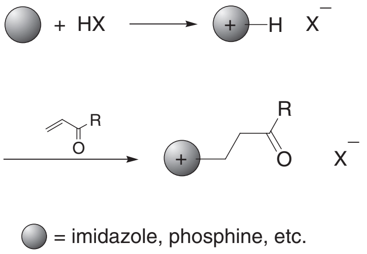
The incorporation of functionality into an IL is usually accomplished by the grafting of preexisting groups onto one of the ion structures.[2,3] Until recently, the method used to do so was almost always the same as that used to form more conventional IL, the displacement of halide from an organic by a parent imidazole, phosphine, etc. (Scheme 2). In the case of TSIL, the organic halide also incorporates the desired functional group. Obviously, this step necessitates the use of organic halides with functional groups that are orthogonally reactive to the reagents and conditions being used in the reaction. Once the initial product is isolated, ion exchange is typically performed to pair the new cation with an anion useful for IL formation. The versatility of this approach has recently been expanded by the use as alkylating agents of mesylate and triflate esters of suitably functionalized organic molecules.[14]

Published on the web (Advance View) August 14, 2004; DOI 10.1246/cl.2004.1072



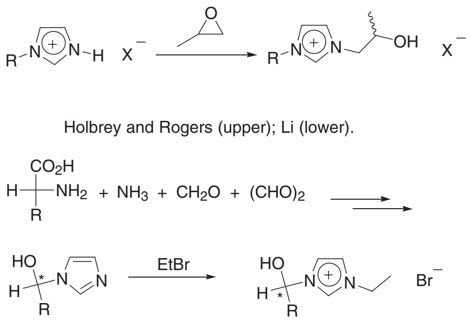
Scheme 2.

Recently, Wasserscheid and co-workers introduced a complimentary method for TSIL synthesis, making use of the Michael reaction (Scheme 3).[15] In this approach, the imidazole or other nucleophile of interest is protonated using the acid form of the anion which will eventually be incorporated into the IL, e.g., $HPF_6 \Rightarrow PF_6^-$. To this salt is added the desired Michael acceptor, which inserts into the N–H (or element–H) bond. The approach is broadly effective, giving TSIL in good yields. Moreover, the procedure dispenses with the need for an anion metathesis step, and provides IL free of halide. The latter is an important factor if the IL is to be used with a transition metal catalyst. The only apparent drawback is the limited thermal stability of the cations, which at moderately elevated temperatures undergo a retro-Michael reaction.



Scheme 3.

At least two alcohol-group specific synthetic approaches have recently been disclosed (Scheme 4).[16,17] In the first, Holbrey and Rogers describe a simple, high-yielding one-pot method for the synthesis of alcohol-appended imidazolium TSIL, a TSIL type previously difficult to prepare cleanly. In the reaction, a pre-formed imidazolium-H salt of the TSIL anion is reacted with an epoxide, the latter ring opening to the alcohol without further alcohol-epoxide oligomerization. The second method built up the imidazolium ring up from a four-component condensation of amino acids, ammonia, formaldehyde, and glyoxal. The latter approach, while multi-step and lower yielding, produced TSIL that were also optically active.



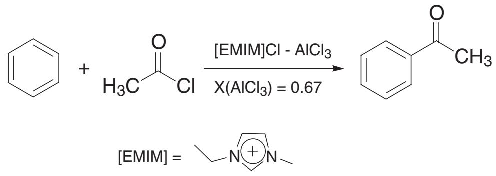
Holbrey and Rogers (upper); Li (lower).

Scheme 4.

Whatever strategy is used to access the desired TSIL, the methods for characterization of the products are the same as those used with conventional ionic liquids. These commonly include multinuclear NMR spectroscopy, FAB or electrospray mass spectrometry, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).[1–4] Also, while the viscosities of TSIL do not appear to have been routinely measured, it is empirically observed that they are higher than those of conventional IL. Given that the functional groups are typically dipolar or are good H-bond donors or acceptors, this outcome is hardly surprising. To counter the effect, TSIL may be "alloyed" with conventional IL, an approach often providing significant improvements in handling properties. Fundamentally, such mixtures constitute binary IL, an area of considerable potential that has scarcely been investigated. Finally, the incorporation of functional groups frequently modifies the molecular solvents with which the IL is miscible. For example, anecdotal evidence from two groups suggests that incorporation of polar groups can diminish the solubility of a TSIL in halogenated hydrocarbons.[18]

♦ TSIL Applications

In a practical sense, the Frankland acidic chloroaluminate salts of imidazolium and pyridinium cations may be regarded as the first real TSIL. Jointly developed by researchers at the United States Air Force Academy and Colorado State University for battery applications, the potentially useful solvation capacity and chemical reactivity of these species soon came to be appreciated as well.[19]

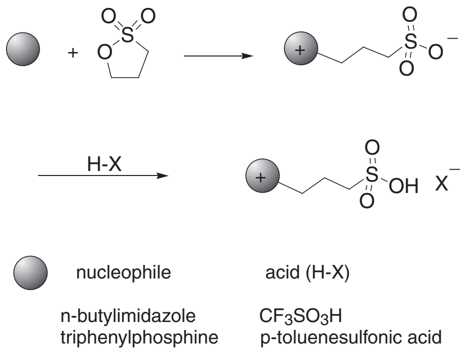


Scheme 5.

Chauvin, Seddon, and others have shown that with appropriate ratios of $Cl^-/AlCl_3$, these materials are powerful solvent-catalysts for a variety of important processes, including Friedel–Crafts chemistry (Scheme 5).[1,2] However, since the chemistry of these IL has been reviewed elsewhere, it will not be further addressed here.

Coincident with the latter research, studies were also done using Brønsted acids dissolved in conventional IL media.[1] In such systems, the use of the ionic liquid provides advantages for product separation, but the added acid is vulnerable to being out-gassed from the IL. Under these conditions, acid vapors remain the same serious drawback which exists when strong acids are used in classical solvents.

In 2002, we described TSIL in which the cations were both intrinsically Brønsted acidic and non-volatile.[20,21] This was done by covalently tethering an alkane sulfonic acid group to the IL cation. The precursors to these materials contain IL-type headgroups covalently linked to alkane sulfonate anions; we note that the syntheses of the imidazolium-type zwitterions were first reported by Ohno in 2001.[22] The realization of the latent acidity



Scheme 6.

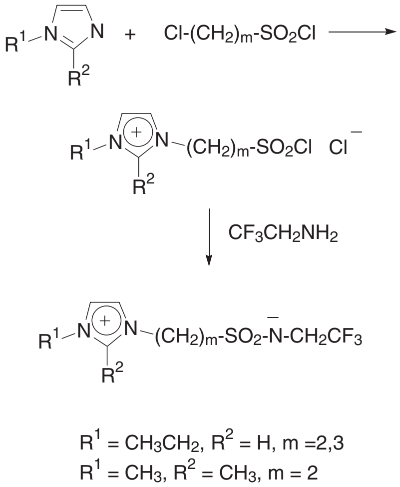
of the zwitterions and their conversion into ionic liquids was accomplished by combining 1:1 molar quantities of the zwitterions with an acid possessing a pK_a sufficiently low to convert the sulfonate group into an alkanesulfonic acid. The result is the transformation of the zwitterion into an IL cation bearing a sulfonic acid group, with the conjugate base of the exogenous acid becoming the IL anion (Scheme 6).

From a practical standpoint, the choice of donor acid used is a significant element in the overall concept. While all strong proton donors are candidates, the use of acids such as triflic acid or bis(triflyl)amine rather than HPF_6 or HBF_4 is preferred due to the hydrolytic instability of the anions of the latter under certain conditions.[20] This instability could lead to the unwanted generation of unbuffered, volatile HF. Hydrolytically unstable acid systems would likely be unsatisfactory alternatives to solid acids in practical applications.

The use of TSIL sulfonic acids to catalyze organic reactions is an area of ongoing activity. In the paper by our group, we showed that the acids were catalysts for Fischer esterification, the dehydrocoupling of alcohols, and the Pinnacol rearrangement.[20] Another intriguing outcome was the discovery of an apparent link between adventitous water in the TSIL and the yield in the Fischer esterification reactions. Follow-up work by Forbes revealed that the systematic introduction of a fixed quantity of water into the system resulted, counterintuitively, in higher ester yields.[23] Further, it was suggested that the water rendered the proton of the sulfonic acid group more chemically available for reaction. This behavior parallels that of Amberlite and Dowex type acid resins, which require some water to function effectively.

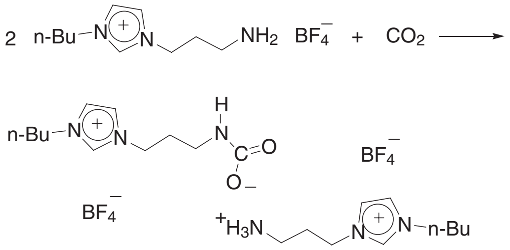
Other groups have recently used the same or similar acid TSILs to catalyze organic reactions. Deng has used sulfonic acid TSIL to catalyze the esterification of acetic acid by 1-heptene and a variety of cyclic olefins.[24] Yields for the esterification reactions range from modest to excellent depending upon the olefinic substrate. Similarly, Shreeve has reported the synthesis of TSIL sulfonic acids with triazolium headgroups.[25] The acid behavior of the salts appears to be analogous to their imidazolium predecessors. The acids were used to catalyze Fischer esterifications and hetero-Michael additions.

Except for their high melting points, the zwitterions used to prepare the TSIL acids would constitute a unique subclass of TSIL. Improving upon these higher-melting zwitterions, Ohno showed that true zwitterionic TSIL can be prepared.[22] Using a two-step synthetic approach, the latter has prepared molecules in which an imidazolium headgroup is covalently tethered to hemi-(fluoroalkane)sulfonamide anion (Scheme 7). The latter anionic group is reminiscent of the bistriflylimide anion [Tf_2N^-, $(CF_3SO_2)_2N^-$], an anion generally observed to yield IL with very low melting points. The new zwitterionic materials were found to be promising ion carriers for electrochemical applications, being themselves unable to migrate along a potential gradient due to their overall neutral charge.



Scheme 7.

The chemical opposites of acidic TSIL —salts containing basic groups— have been reported as well. In this case, Davis and co-workers reported in 2002 an imidazolium type ionic liquid containing a tethered amine group.[26] In that paper, the use of the salt for the reactive capture of CO_2 was also described (Scheme 8). Using ^{13}C NMR, the mechanism of capture was shown to be via the formation of a TSIL-ammonium carbamate double salt. This mechanism is the same as is observed with molecular amines that are used commercially for the removal of CO_2 from crude natural gas streams. Unlike the commercial scrubbing agents, the TSIL function without water as a co-solvent, and cannot be lost into the gas stream.



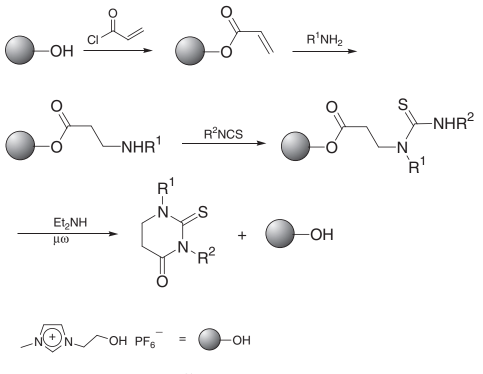
Scheme 8.

Many conventional IL are immiscible with water, so their use in creating biphasic systems has attracted interest, especially for separations purposes. While it might be expected that metal ions in water would readily move into an immiscible medium (IL) composed solely of ions, this has not generally been the case. In an effort to increase the partition of metal ions into IL phases, Rogers and Davis reported in 2001 the use of urea- and thiourea functionalized TSIL to remove Hg^{2+} and Cd^{2+} from a contacted aqueous phase.[27,28] The results indicated that partition ratios of up to 300 were achievable with these TSIL, versus <20 when the conventional IL 1-butyl-3-methylimidazolium hexafluorophosphate was used. The putative mechanism for the transfer involves displacement of water from the coordination sphere of the metal ions by the Lewis basic S and O atoms of the TSIL functional groups. Later work by Rogers demonstrated that TSIL oligoethers with linked imidazolium headgroups effected the selective, pH dependent removal of Hg^{2+} from water in the presence of Cd^{2+}.[29]

In synthetic applications, Wasserscheid has shown that the use of phosphine ligands bearing a charged auxiliary dissolve efficiently in ionic liquids and suppress the loss of precious metal catalysts in biphasic hydroformylation reactions.[30,31] These solvent systems may be regarded as a type of binary IL, the catalyst-ligand complex remaining anchored in the bulk IL by virtue of the electrostatic potential between the two. This approach to IL phase catalysis has also been investigated by Lee and Shreeve.[32,33] The former reported a binary TSIL system which features a charged chiral ligand–metal complex useful in catalytic asymmetric hydrogenation. The latter used a complex polycationic triazinyl ligand-IL mixture in the hydroformylation of 1-octene.

Metals and TSIL have been the subject of other investigations as well. Dyson, Welton, and Raubenheimer have all reported TSIL in which one of the ions is a transition metal organometallic complex.[34–36] Very recently, Naka, Chujo, and Lee have reported using TSIL to stabilize gold nanoparticles.[37,38] In one case, the TSIL incorporated an imidazolium alkane thiol cation, while the other utilized imidazolium polyols to achieve the stabilization.

One of the most elegant applications of functionalized IL has been pioneered by Bazureau. The latter has used TSIL as supports for organic synthesis in an approach analogous to solid phase synthesis (SPOS).[39–43] Called ionic liquid phase organic synthesis (IoLiPOS), this technique has been used to prepare a number of different medicinally-relevant heterocycle types. In the most recent example, TSIL alcohols were used as supports for the multi-step synthesis of 2-thioxotetrahydropyrimidin-4(*1H*)-ones, providing the products in high yields (Scheme 9).[43] In addition to possible substrate activation by the ionic milieu, the ionic nature of the supporting group is found to facilitate its easy separation from the neutral end products once they are cleaved from the support. The IoLiPOS approach has recently been extended by Chan, who has shown it to be compatible with metal-catalyzed transformations, specifically the Suzuki coupling.[44]



Scheme 9.

While polyfluorinated anions have been important elements of IL chemistry for some time, the development of TSIL with cations possessing a high fluorine content has also been an active area of research. In a patent from 1998, Koch claimed the synthesis of imidazolium-type ionic liquids in which both the ring carbon atoms and the N-alkyl groups were perfluorinated. Aside from a description of these materials as "liquid teflon," no further information was provided.[45]

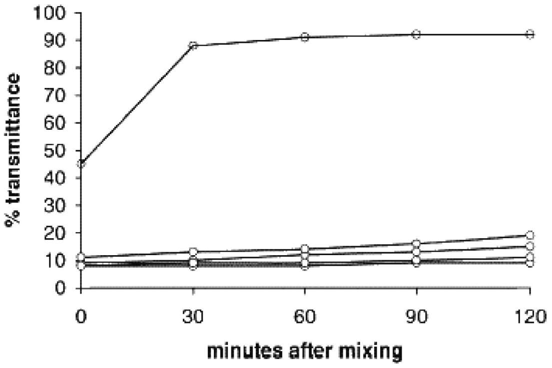


Figure 4.

In 2001, we described a set of polyfluorinated imidazolium ILs in which the total fluorine content was notably higher than in the ILs described by Koch, but in which the fluorine was confined to one region of the cation, a long "ponytail" attached to a ring N.[46] As illustrated in Figure 4, it was found that the addition of 5 mol % of the fluorinated TSIL to a conventional IL enabled creation of highly stable IL/perfluorocarbon emulsions (lower traces), while emulsions in the conventional IL alone quickly decayed (upper trace). Some of the emulsions were stable for months.

Subsequent studies have reported a number of similar ILs in which the range of cationic headgroups was expanded to include triazole rings and other cores, and the organofluorine appendage lengths were varied.[47–49] In one paper it was reported that the inclusion of a fluorous tail increased O_2 solubility in the IL as well as imparting to the TSIL a high degree of stability towards superoxide.[47] Another recent development in this area was the synthesis of new salts in which the typical perfluoralkyl chain is terminated by an SF_5 group.[49] The addition of this group increases the density of the resulting ILs, and thermal applications may be possible given the use of SF_6 in gas-phase thermal insulation applications.

Summary and Outlook

Task-specific ionic liquids are a unique subclass of ionic liquids which possess a potential spectrum of utility extending far beyond that likely for more conventional IL. By virtue of the incorporated functional groups, these unique salts can act not only as solvents but as catalysts and reagents in an array of synthetic, separations and electrochemical applications. As has been the case for conventional ionic liquids, the number of applications is likely to continue to expand. Already the number of known TSIL and demonstrated applications for them has exploded, making it impossible to mention them all in this brief overview.

Nevertheless, it is my hope that I have succeeded in showcasing some of the highlights of this exciting area, giving the reader a reasonable idea of the types of functional ionic liquids which have been prepared, and the range of their possible applications. Further, it is my hope that others will be inspired to bring their energies and imaginations to this exciting field.

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