Ether- and Alcohol-Functionalized Task-Specific Ionic Liquids: Attractive Properties and Applications

Shaokun Tang[a], **Gary A. Baker**[b], and **Hua Zhao**[*,c]

[a]Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China

[b]Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA

[c]Chemistry Program, Savannah State University, Savannah, GA 31404, USA

Abstract

In recent years, the designer nature of ionic liquids (ILs) has driven their exploration and exploitation in countless fields among the physical and chemical sciences. A fair measure of the tremendous attention placed on these fluids has been attributed to their inherent designer nature. And yet, there are relatively few examples of reviews which emphasize this vital aspect in an exhaustive or meaningful way. In this *critical review*, we systematically survey the physicochemical properties of the collective library of ether- and alcohol-functionalized ILs, highlighting the impact of ionic structure on features such as viscosity, phase behavior/transitions, density, thermostability, electrochemical properties, and polarity (*e.g.*, hydrophilicity, hydrogen bonding capability). In the latter portions of this review, we emphasize the attractive applications of these functionalized ILs across a range of disciplines, including their use as electrolytes or functional fluids for electrochemistry, extractions, biphasic systems, gas separations, carbon capture, carbohydrate dissolution (particularly, the (ligno)celluloses), polymer chemistry, antimicrobial and antielectrostatic agents, organic synthesis, biomolecular stabilization and activation, and nanoscience. Finally, this review discusses anion-functionalized ILs, including sulfur- and oxygen-functionalized analogs, as well as choline-based deep eutectic solvents (DESs), an emerging class of fluids which can be sensibly categorized as semi-molecular cousins to the IL. Finally, the toxicity and biodegradability of ether- and alcohol-functionalized ILs are discussed and cautiously evaluated in light of recent reports. By carefully summarizing literature examples on the properties and applications of oxy-functional designer ILs up till now, it is our intent that this review offer a barometer for gauging future advances in the field as well as a trigger to spur further contemplation of these seemingly inexhaustible and—relative to their potential—virtually untouched fluids. It is abundantly clear that these remarkable fluidic materials are here to stay, just as certain design rules are slowly beginning to emerge. However, in fairness, serendipity also still plays an undeniable role, highlighting the need for both expanded *in silico* studies and a beacon to attract bright, young researchers to the field.

[*]Corresponding author. huazhao98@gmail.com (or zhaoh@savannahstate.edu).

1. Introduction

Ionic liquids (ILs) have been known for some time, but heavy research efforts on this diverse class of solvent have experienced a tremendous explosion within the last decade. Consisting of organic salts engineered to melt at low temperatures (*i.e.*, below 100 °C and, commonly, even below ambient temperature), ILs frequently share a number of attractive properties that distinguish them from conventional organic solvents, such as low (and even effectively-null) vapor pressure, a wide liquid range, low flammability, high conductivity (e.g., ionic, thermal), excellent stability (e.g., thermal, chemical, redox, radiochemical), a wide electrochemical potential window, and the ability to act as surprisingly good solvents towards many substances, such as asphalt and recalcitrant biopolymers (e.g., silk, cellulose). Because of these favorable properties, ILs are being increasingly studied and tested as solvents or catalysts in a variety of applications including organic catalysis,[1–5] inorganic and materials synthesis,[6] biocatalysis,[7–12] electrochemistry,[13] pharmaceutical chemistry,[14] polymerization,[15, 16] and as engineering fluids.[17–19]

ILs offer a unique architectural platform on which the properties of both the cation and the anion can be independently modified, enabling tunability in the design of new functional solvents or materials, often whilst retaining the desired features delivered by the parent ions of the IL in the first place. This concept, perhaps more than any other, has accounted for the unstoppable popularity of ILs across innumerable disciplines in science, technology, and engineering. Indeed, even within this renaissance in solvent, green, and advanced materials chemistry, the stage is already set for subsequent waves of activity as researchers begin to unravel the design rules of ILs 'built for purpose'. Professor James H. Davis (Univ. S. Alabama) appropriately coined the term 'task-specific ionic liquids' (TSILs) to account for this inherent designer nature of ILs.

The notion of TSILs carrying specific functionality tailored for certain applications has proven visionary, and an impressive catalog of TSILs with pendant acid, base, alcohol, or ether groups on one (or both) of the ions represents particularly fertile ground.[20, 21] Of historical relevance, poly(ethylene oxide)s (PEOs) (also known as poly(ethylene glycol)s, PEGs) have been incorporated into cationic (or anionic) units to yield the liquid state of ion-conductive polymers.[13, 22–24] Along these lines, there is a rising interest in functionalizing ILs by grafting ether or hydroxyl groups to IL cations based on countless onium ions, including imidazolium,[25–35] pyridinium,[36] quaternary ammonium,[37–41] phosphonium,[40, 42] piperidinium,[39, 43] pyrrolidinium,[43, 44] guanidinium,[45] sulfonium,[46] oxazolidinium,[43] and morpholinium[43] types. In a short period, these functionalized ILs have demonstrated attractive physicochemical properties and applications in several exciting areas, dictating a systematic analysis, review, and discussion of the abundant information now available. While a handful of scattered reviews on TSILs (or, simply, functionalized ILs) exist,[20, 23, 47] we felt that a more timely and comprehensive review was warranted.

We have limited the scope of this *critical review* to focus only on ILs consisting of cations functionalized by ether or alcohol groups, plus the emergent class of deep-eutectic solvents (DESs) based around the choline cation. We have also included a limited discussion of ILs comprising sulfur- or oxygen-functionalized anions (*i.e.*, carboxylic acids, esters). However, for purposes of manageability, this review excludes any in-depth look at ILs having oxygen embedded within the cation ring itself (*i.e.*, oxazolidinium, morpholinium), or those containing simple oxygen-containing anions (*i.e.*, triflate, bis(trifluoromethylsulfonyl)imide, acetate, formate, alkylsulfate, alkylphosphate).

2. Preparation of Ether- and Hydroxyl-Functionalized ILs

This section highlights typical methods for grafting alkoxyl or hydroxyl groups onto core ionic units comprising ILs.

(1) Quaternization with halogenated ethers or alcohols

Perhaps the simplest and most straightforward method for grafting ether- or alcohol-bearing chains onto IL cations is through a quaternization reaction between amines (or *N*-heterocycles, phosphines, and so forth) and oxygen-bearing alkyl halides (Scheme 1) under reflux conditions in a suitable organic solvent such as acetonitrile, tetrahydrofuran (THF), dimethylformamide (DMF), or methanol.[48–50] Some quaternization reactions that are problematic in classical organic solvents can be successfully carried out under solventless conditions with simple application of heat.[51–53] By comparison, the quaternization of phosphines to generate phosphonium salts sometimes requires more aggressive reaction conditions, such as 120 °C for 72 h under solvent-free conditions.[54] Many simple oxygen-containing alkyl halides are readily available from commercial sources.[27, 48, 50, 52, 53] Additionally, a number of alkyl halides bearing oxygen functionality are accessible from synthetic methods employing thionyl chloride,[32, 55, 56] PCl_3,[57, 58] or PBr_3[59, 60] under strict anhydrous conditions, although this is not suitable for all glycols of interest.

(2) Sulfonation, quaternization, and metathesis

Another popular method for generating ether-bearing cations useful in preparing functionalized ILs entails the initial preparation of sulfonate esters of glycols via reaction of glycols with methanesulfonyl chloride, *p*-toluenesulfonyl chloride, or benzenesulfonyl chloride as shown in Scheme 2. Since sulfonates are excellent leaving groups under S_N2 conditions, nucleophilic amines or *N*-heterocycles can easily substitute these leaving groups by forming a glycol-substituted ionic salt, which may be further converted to the desired IL *via* a subsequent metathesis step.

(3) Tosylation, iodination, and quaternization

As shown in Scheme 3, this method[49] involves three major steps: (a) sulfonation of a PEG monoether to produce a sulfonate ester, (b) nucleophilic substitution of sulfonate group by iodide, and (c) nucleophilic substitution of iodide by alkylimidazoles (or amines). Despite the long reaction times required, this approach has proven very effective for grafting long-chain PEGs containing up to 16 ethylene oxide units to alkylimidazoles.

(4) Tosylation, alkylation via the imidazole anion, and quaternization

In this method, PEG[68, 69] (or PEG monomethyl ether[70]) is first converted to a tosylate, followed by reaction with a nucleophilic imidazole anion. The PEG-substituted imidazole can then be further alkylated to prepare the desired IL, as illustrated in Scheme 4. The first step of this scheme is also suitable for preparing ditosylates, which are useful intermediates for synthesizing geminal di-imidazolium (dicationic) ILs.[68, 69]

Similarly, Zhi et al.[71] prepared a PEG-1000-grafted dicationic IL through a two-step route involving the nucleophilic substitution of an alkyl halide by imidazole anion with a subsequent quaternization of the terminal imidazole units with 1,3-propane sultone, a cyclic sulfonate ester commonly used as a strong alkylating agent to introduce a negatively-charged sulfonate group (Scheme 5). A similar approach has also been used in the preparation of PEG-functionalized dicationic ILs carrying bis(trifluoromethylsulfonyl)imide (Tf_2N^-) anions.[60, 69]

(5) Etherification, quaternization, and metathesis

This method involves the etherification of an alkyl halide using NaH followed by quaternization and metathesis steps, exemplified by the morpholinium preparation of Scheme 6.[72]

(6) Amine quaternization plus N-alkoxymethylation of imidazole

In this method, a quaternary ammonium salt is formed first *via* an alkylation reaction followed by the *N*-alkoxymethylation of imidazole. The alkoxyl-substituted imidazole is then further quaternized to form the desired ionic salt (Scheme 7).[73]

(7) Photoaddition

O'Brien et al.[74] recently carried out the photoaddition of 1-thioglycerol to *ene*-type imidazolium salts *via* thiol–ene "click" chemistry (Scheme 8). The reaction was initiated by 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photo-initiator using a photochemical irradiation system. Through this method, ILs carrying vinyl or allyl groups can be effectively functionalized with multiple hydroxyl groups.

(8) Propylene oxide method

Holbrey et al.[75] carried out a one-pot reaction of 1-methylimidazole and acid with propylene oxide to prepare hydroxylated ILs such as 1-(2-hydroxypropyl)-3-methylimidazoliums (Scheme 9). Although this method is limited to the synthesis of certain types of ILs, the atom-efficient reaction route is promising in that it generates no waste other than the required solvents (ethanol and water) and excess epoxide, which can, in principle, be recycled and reused.

If the goal is to prepare inexpensive glycol-grafted ILs, halogenated ethers and alcohols would represent relatively poor (*i.e.*, costly) choices as starting materials, of course. Short-chained glycols, such as PEGs ranging from ethylene glycol to tetraethylene glycol, as well as their monoethers, are currently available in high purity and at reasonable cost, although pure compounds of the longer-chain glycols are becoming quite expensive. An alternative approach is to use commercial grades of inexpensive PEG mixtures which might contain various nominal molecular weight materials (*e.g.*, PEG-200, 300, 400, and so on), although one should be aware that the resulting ILs will represent ionic mixtures whose particular properties will depend upon the distribution of glycols present. However, for a great many applications, such mixtures would provide viable, attractive, and inexpensive ILs, especially considering the favorable economics of scale up. It should additionally be noted that, although much less studied than their PEG counterparts, poly(propylene glycol)-functionalized ILs are also interesting targets for future investigation.

3. Physicochemical Properties of Ether- and Hydroxyl-Functionalized ILs

3.1 Viscosity and structural flexibility

The viscosity of an IL at a fixed temperature is a function of both the cation and anion structure. Elongation of the cation's alkyl chain generally leads to an increase in viscosity. Increased IL viscosity is also associated with lower anion symmetry such as $(CN)_2N^- <$ $Tf_2N^- < BF_4^- < PF_6^- < OAc^- < Cl^-$.[76–78]

The grafting of alkyloxy or alkyloxyalkyl groups onto IL cations typically leads to a reduction in viscosity. For instance, ILs with tetraalkylammonium-based cations containing a methoxyethyl group ($CH_3OCH_2CH_2$—) tend to have lower viscosities than similar structures with cations containing only alkyl-based groups regardless of the anion (Tf_2N^-, $CF_3BF_3^-$, $C_2F_5BF_3^-$) (see Table 1);[38, 40] Among ether-grafted ILs, smaller cations tend to

have even lower viscosities due to the decrease in van der Waals interactions.[38] For ILs containing dimethylphosphate anions, the attachment of a long ether chain (*e.g.*, 2–3 ether oxygen atoms) to the imidazolium cation causes a reduction in viscosity (**50** *vs.* **49** in Table 1), while a shorter ether chain (1 ether oxygen atom) shows no reduction (**48** *vs.* **47**); thus, the observed trend is that viscosity decreases with increasing ether chain length (**48 > 50 > 51**).[31] A study by Ganapatibhotla et al.[49] of imidazolium ILs containing a long chain PEG monomethyl ether (7–16 oxygen atoms on average) demonstrated further that ether-functionalized ILs have lower viscosities than alkyl-substituted ones. The same viscosity reduction trend has been observed for ether-functionalized ILs based on other cations such as pyrrolidinium, piperidinium, oxazolidinium and morpholinium,[43, 44, 79, 80] ammonium and piperidinium,[39, 41, 81] phosphonium,[81, 82] as well as guanidinium.[45, 83, 84] Interestingly, guanidinium ILs containing an ester group have considerably higher viscosities than ether-grafted ILs (~300 *vs.* ~60 mPa s).[45] However, the incorporation of more than one ether chain (2, 3 or 4) in the cation is ineffective in further lowering the IL viscosity,[50, 84, 85] with the exception of dialkoxy-functionalized quaternary ammonium ILs.[86] Petiot et al.[59] observed a relatively high viscosity (2,230 mPa s at 25 °C) of a dimethylammonium bromide-based IL containing two PEG-350 methyl ether chains. While the anion may in part be promoting the high viscosity, the multiple ether chains, leading to a more symmetric, less flexible and larger cation as compared to a single ether chain, may indeed be another contributing factor. Interestingly, the reduction in frequency-dependent (5–205 MHz) shear viscosities has also been observed for ether-functionalized ILs: the substitution of a (2-ethoxyethoxy)ethyl group for an octyl group in ammonium and phosphonium cations results in decreased shear viscosities.[87]

Notably, for some alkyl-substituted ILs with low viscosities (such as imidazoliums paired with perfluoroalkyltrifluoroborate anions), the grafting of ether groups results in a marginal reduction or even an increase in viscosity, *i.e.*, $[C_4MIM][CF_3BF_3]$ (49 mPa s at 25°C) *vs.* $[C_3OMIM][CF_3BF_3]$ (43 mPa s), and $[C_3MIM][CF_3BF_3]$ (43 mPa s) *vs.* $[C_2OMIM][CF_3BF_3]$ (55 mPa s).[35] Bulut et al.[88] also indicated that a mild functionalization (such as only incorporating one ether group) of ILs has a minimal impact on the viscosity and conductivity with these properties following changes in molecular volume. The incorporation of alkyloxy or alkyloxyalkyl groups in cations of BF_4^--based ILs may even cause a higher viscosity than alkyl analogues, such as $[CH_3OCH_2CH_2-MIM][BF_4]$ (263 mPa s at 20 °C)[26] *vs.* $[BMIM][BF_4]$ (105 mPa s [26] or 154 mPa s)[76]. There are also conflicting results regarding the viscosity. For example, Zhou et al.[38] reported the viscosity of $[CH_3OCH_2CH_2-Me-Et_2N][BF_4]$ as 426 mPa s at 25 °C, while Sato et al.[89] obtained a viscosity of the same IL as 1200 mPa s at room temperature. Such discrepancies in viscosity may be due to the presence of contaminants, particularly water, underlying the importance of IL purity when reporting the physicochemical properties of ILs.

Molecular dynamic simulations offer insight into the low viscosity induced by the incorporation of alkoxy chains (over alkyl chains). Here, results suggest the low viscosity arises from the less effective assembly between the more flexible alkoxy chains resulting in less aggregation/interaction of the chains of neighboring cations rather than any change on ionic pairing.[99] Along the same line, Nogrady and Burgen[100] measured the proton magnetic relaxation rates of *N*-methyl protons of aliphatic ammonium salts in D_2O and found lower relaxation rates for methoxy or acetoxy derivatives than predicted based on a rigid model suggesting the oxygencontaining substituents have more freedom for axial rotation than alkyl groups. Molecular simulations also suggest the reduction in intermolecular correlation (particularly tail–tail segregation) and cation–anion electrostatic interactions due to the incorporation of ether chains (with electron-donating properties) is responsible for the faster dynamics observed in ether-functionalized imidazolium ILs compared to their alkyl analogs.[101] Raman-induced Kerr spectroscopy studies[80, 81] reveal that the larger ionic

volume of ether-substitution causes a weaker interionic interaction; however, the ether group itself induces a stronger interionic interaction but is more flexible nature having a faster reorientation than the alkyl group. A more recent study[102] suggests that cations of imidazolium and pyridinium form stable complexes with PEG-800 or PEG-1000 *via* an ion-dipole interaction where the cations are wrapped by PEG chains. Thus, ILs containing long and flexible alkoxy chains are expected to have reduced Coulombic interactions between the cation and anion.[49]

In contrast to ether-functionalization, the appending of hydroxyl groups to the cation usually increases the IL viscosity (as shown by the comparison of these ILs in Table 1, **10** *vs.* **55**, **2** *vs.* **56**, **57** *vs.* **58**, **59** *vs.* **60**, and **61** *vs.* **62**).[91] Restolho et al.[103] observed higher viscosities for [(HO-CH_2CH_2)-MIM][BF_4] as compared to [OMIM][BF_4] in the temperature range of 293.15– 328.15 K. Deng et al.[104] observed a moderate increase in viscosity upon the inclusion of a hydroxyl group to pyridinium- or ammonium-based ILs. The hydroxyl groups likely form an intermolecular hydrogen-bond network contributing to the increased viscosity.[74, 79, 105] As pointed out by Ma et al.[106] using femtosecond time-resolved depleted spontaneous emission, the hydroxyl groups in IL cations induce an enhancement of local microviscosity leading to slow solvation and rotation dynamics of the probe molecule rhodamine 700 in the ILs studied. In addition, the longer the hydroxyl-terminated PEG chain, the higher the IL viscosity due to stronger van der Waals interactions in addition to hydrogen bonding, such as examples in Table 1 including (in increasing order of viscosity): **63 < 64 < 65**, **66 < 67 < 68**, **69 < 70 < 71**.[27] An unusual anion effect on viscosity is illustrated by the ILs **63–71**. Here, for the same cation, the IL viscosity decreases with the type of anion in the order of $Tf_2N^- > PF_6^- > BF_4^-$, in contrast to alkyl- or ether-substituted ILs where Tf_2N^--based ILs are the least viscous among these anions. A logical explanation is that the side-chain hydroxyl group in the IL cation interacts strongly with the Tf_2N^- anion (see the example of PEG interactions with lithium salts LiX[107]) due to the higher basicity of Tf_2N^- as compared to BF_4^- and PF_6^-.[108, 109] Therefore, to reduce the viscosity of an oxygen-functionalized IL, an alkoxyalkyl side chain of moderate length is preferred over a hydroxyl-containing side chain.

To further examine the effect of different cation species on the viscosity of etherfunctionalized ILs, we compare a number of these ILs (**30–45** in Table 1) having similar cation size and the same anions ($C_2F_5BF_3^-$ or Tf_2N^-). The general trend uncovered in the order of increasing viscosity is: phosphonium, imidazolium, pyrrolidinium, guanidinium < ammonium < oxazolidinium, piperidinium < morpholinium, which is consistent with that of nonfunctionalized ILs.[110] Similarly, a general trend based on the anions can be generated from Table 1 in the order of increasing viscosity as follows: Tf_2N^-, $C_2F_5BF_3^-$, $CF_3BF_3^- < BF_4^- < PF_6^- < OAc^- < Me_2PO_4^- < Cl^-$, which also matches that of non-functionalized ILs.[110]

It is also known that acetate-based ILs tend to have lower melting points and viscosities than their halide analogues,[67, 78] and formate anions can result in even lower viscosities.[105] Other anions known to produce low IL viscosities (some even below 20 mPa s at room temperature), include dicyanamide [$N(CN)_2^-$ or dca$^-$],[78, 111] tricyanomethanide [$C(CN)_3^-$ or TCM$^-$],[112, 113] tetracyanoborate [$B(CN)_4^-$][114, 115] and thiocyanate (SCN$^-$).[116] It is important to point out that while these represent some general trends, there are always exceptions.

3.2 Phase transition and density

The melting point temperature (T_m) of an IL is determined by the strength of its crystal lattice, which is dependent on the symmetry of cation and anion, the cation–anion interaction and the conformational degrees of freedom of the cation and anion.[49, 85, 117–119]

The inclusion of alkyloxy or alkyloxyalkyl groups in ILs often lowers the T_m.[38, 40, 43, 44] Examples of this include [mPEG12-Me-Im]I (T_m = 7 °C) *vs.* [EMIM]I (T_m = 81.5 °C);[49] [CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][BF$_4$] (T_m = 8 °C) *vs.* [Bu-Et$_2$-MeN][BF$_4$] (T_m = 165 °C); [CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][CF$_3$BF$_3$] (T_m = −22 °C) *vs.* [Bu-Et$_2$-MeN][CF$_3$BF$_3$] (T_m = −3 °C);[38] and [CH$_3$OCH$_2$-Me$_3$N][Tf$_2$N] (T_m = 4.5 °C) *vs.* [CH$_3$CH$_2$CH$_2$-Me$_3$N][Tf$_2$N] (T_m = 19 °C).[39] Additionally, the lowering of the glass transition point, T_g, is observed in ILs with no T_m.[34, 38, 39] The likely explanation for the observed T_m and T_g depression due to ether group incorporation is that the high chain flexibility predominates over the high polarity of the ether group.[38] The complete disappearance of crystallinity and the decrease in T_m of ILs are caused by both the higher rotational freedom of the ether chain and the reduced lattice energy of the ILs. It is well known that many ILs (including imidazolium, ammonium, and pyridinium salts) display substantial supercooling, with freezing points typically 40–60 °C lower than the corresponding melting points.[120–122] This supercooling phenomenon makes it challenging to precisely determine the IL freezing and/or melting points.[123] Meanwhile, it is important to note that low T_g values do not always lead to low fluidities due to "fragility" (*i.e.*, the rate at which the transport properties change with temperature near T_g).[124]

In some cases, the incorporation of ether side chains in the cation induces the opposite effect, a melting point increase. Zhou et al.[35] observed a T_m increase in several examples: [C$_3$MIM][CF$_3$BF$_3$] (−21 °C) *vs.* [C$_2$OMIM][CF$_3$BF$_3$] (17 °C), [C$_3$MIM][C$_2$F$_5$BF$_3$] (−42 °C) *vs.* [C$_2$OMIM][C$_2$F$_5$BF$_3$] (−21 °C), and [C$_4$MIM][C$_2$F$_5$BF$_3$] (−42 °C) *vs.* [C$_3$OMIM][C$_2$F$_5$BF$_3$] (−9 °C). Their explanation was the polarity effect of the ether chain overtakes the chain flexibility as the predominating factor. Fei et al.[125] studied a series of ether-derivatized imidazolium halides and suggested the ether functionalization renders no reduction in IL T_m or viscosity. Henderson et al.[126] reported that 1-(2-methoxyethyl)-2,3-dimethylimidazolium Cl$^−$ and PF$_6^−$ salts have higher melting points than the corresponding 1-butyl-2,3-dimethylimidazolium salts due to the repulsion between neighboring ether oxygen atoms or anions causing noticeable ion crystal packing rearrangements based on their crystal structures studies.

IL density is primarily determined by two important factors: cation–anion interaction and molecular packing.[34] Typically, the IL anion strongly impacts the IL density, and the density generally increases in the order of Cl$^−$ < BF$_4^−$ < PF$_6^−$ < Tf$_2$N$^−$ < I$^−$ [49] and CH$_3$SO$_3^−$ < BF$_4^−$ < PF$_6$.[34] A relatively long ether chain (*e.g.*, more than 3 oxygen atoms) can reduce the IL density,[34, 49] but a shorter ether chain has no such effect.[34, 76] Further, the incorporation of a short ether chain can even increase the IL density.[35, 38] In general, IL density decreases with an increase in the length of the ether side chain,[49] consistent with the alkyl-substituted analogue ILs.[127] While the effect is not always significant,[104] hydroxyl groups on cations often increase the IL density due to interionic hydrogen bonding.[105]

3.3 Thermal stability

Thermal decomposition of quaternary ammonium salts occur by two types of mechanisms: reverse Menschutkin and Hofmann reactions.[128] The first step of the pyrolysis of imidazolium and other cyclic quaternary ammonium salts involves the cleavage of *N*-substituted groups by nucleophilic attack of anions to form the corresponding amines,[129, 130] especially in the presence of more nucleophilic anions like acetate.[86] Short-chain-ether-functionalized ILs tend to be less thermally stable than their corresponding alkyl-substituted analogues,[34, 35, 38, 43, 52] most likely due to the weakened cation–anion electrostatic interaction freeing the anions to act as nucleophiles. For example, the decomposition temperature (T_d) of [EtO(CH$_2$)$_2$MMIm][Tf$_2$N] is 405 °C, whilst [BMMIm][Tf$_2$N] has a higher T_d value of 430 °C; the same trend is true for morpholinium-based ILs[52] and tertiary sulfoniums.[46] Exceptions to this general rule include *N*-alkoxyalkyl and *N*-fluoroalkoxyalkyl substituted morpholinium ILs which have an increased thermal stability

over their alkyl or fluoroalkyl substituted analogues.[72] Incorporating short to moderate length ether chains (2–4 ether groups) to quaternary ammonium or guanidinium cations leads to even worse thermal stability than those with one or no ether groups.[50, 84, 85] There are, again, exceptions to this general rule. For instance, guanidinium[45, 83] and phosphonium[40] ILs containing these types of ether chains have comparable or slightly higher T_d values than the corresponding alkyl-substituted ILs (although guanidinium ILs containing an ester group were found less thermally stable[45, 83]). However, imidazolium ILs containing very long ether chain (7– 16 oxygen atoms) have higher thermal stability than alkyl-substituted salts, *e.g.*, [mPEG16-Me-Im]I (containing 16 oxygen atoms) has a higher T_d of 284 °C as compared to that of [EMIM]I (264 °C).[49] This was explained by the enhanced intermolecular interactions in the ILs carrying a long ether chain: despite the reduction in electrostatic interaction between the cation and anion due to the shielding of ether chain, strong van der Waals interactions are expected to exist between the polar ether chains. Additionally, due to the wrapping of long ether chain around the cation,[102] the nucleophilic attack on the imidazolium ring leading to degradation may be hindered. On the contrary, ILs with a short ether chain do not enjoy such benefits of enhanced intermolecular interactions. As a result, short ether chain-functionalized ILs are less thermally stable, particularly in the presence of more than one alkoxy chain.[86] Furthermore, the thermal stability of ether-functionalized ILs is strongly dependent on the type of anion (*e.g.*, a decreasing stability in the order of $BF_4^- > CH_3SO_3^- > PF_6^-$).[34]

3.4 Electrochemical properties

The ionic conductivity of an IL is mainly controlled by its viscosity (known as the Walden plot), density, formula weight, and size of the cation and anion.[90] Due to the lower viscosities of ether-functionalized ILs, these liquids tend to have higher specific conductivities at 25 °C than alkyl-substituted ILs, such as [CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][Tf$_2$N] (2.6 mS/cm) *vs.* [Bu-Et$_2$-MeN][Tf$_2$N] (1.6 mS/cm) and [CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][CF$_3$BF$_3$] (3.0 mS/cm) *vs.* [Bu-Et$_2$-[MeN][CF$_3$BF$_3$] (2.1 mS/cm).[38] Another excellent example was illustrated by Donato et al.[131] as: [Me(OCH$_2$CH$_2$)$_3$-MIM][BF$_4$] *vs.* [C$_{10}$MIM][BF$_4$] (0.874 mS/cm *vs.* 0.337 mS/cm at 25 °C), and [MeOCH$_2$CH$_2$-MIM][BF$_4$] *vs.* [BMIM][BF$_4$] (0.950 mS/cm *vs.* 0.00124 mS/cm at 25 °C). The same conductivity increase trend was observed for ether-functionalized ILs based on imidazolium cations,[52] pyrrolidinium, piperidinium, oxazolidinium, or morpholinium cations,[43] phosphonium and ammonium cations,[40, 41, 86] as well as guanidinium cations.[45, 83] Although [EMIM]I showed a high ionic conductivity at temperatures above 50 °C, long ether chain-grafted ILs exhibited an even higher conductivity at room temperature than that of [EMIM]I, which is attributed to the lower viscosity and better solvation of I$^-$ anions in ether-derived ILs. In addition, these ether-functionalized ILs displayed higher resistance against cathodic reduction than alkylsubstituted ILs due to the protective wrapping of long ether-side-chain around the cation.[49] Therefore, these ether-functionalized imidazolium iodides are potentially ideal electrolytes for electrochemical devices such as dye-sensitized solar cells (DSSCs). However, when introducing two, three or four ether groups to the quaternary ammonium salts, lower conductivities (and similar/higher viscosities) were observed over ammonium salts carrying no or one ether group.[50, 85] But if the incorporation of more than one alkoxy group to the IL cation leads to a viscosity reduction, an increase in conductivity is expected.[86] The reasonable explanation to this could be the stronger van der Waals interactions for larger cations and lower cation symmetry. On the other hand, the ether-functionalization and lower viscosity does not always lead to higher conductivity. For example, methoxymethyl ethyl dimethylammonium tetrafluoroborate ([CH$_3$OCH$_2$-Et-Me$_2$N][BF$_4$]) is considered a poor ion conductor based on the Walden plot because this IL has an order of magnitude lower conductivity than ideal.[124]

The electrochemical stability is also affected by the incorporation of ether groups. Grafting one or multiple short-chain ether groups in quaternary ammonium, cyclic quaternary ammonium, or sulfonium ILs generally leads to reduced electrochemical stability, but with the electrochemical windows still being sufficiently high (usually > 4.0 V) for practical uses as electrolytes.[38–41, 43, 44, 46, 85] For example, [Me(OCH_2CH_2)_3-MIM][BF_4] has a smaller electrochemical window than [C_{10}MIM][BF_4] (1.23 V *vs.* 2.00 V at 25 °C); [MeOCH_2CH_2-MIM][BF_4] also has a smaller electrochemical window than [BMIM][BF_4] (1.01 V *vs.* 1.66 V at 25 °C).[131] Chen et al.[86] argued that the incorporation of a second alkoxy group to the quaternary ammonium cation caused no negative impact on the electrochemical stability of the resulting ILs. The electrochemical potential windows of quaternary ammonium salts tend to be wider than that of the imidazolium type.[41] The electrochemical stability of guanidinium ILs was not influenced greatly by the incorporation of ether groups.[45, 83] Liao et al.[132] observed that the grafting of an ether group (–CH_2OCH_2CH_2CH_2CH_3) at the C-2 position of 1-propyl-3-methylimidazolium could improve its reduction stability and achieve a very low solid electrolyte interfacial resistance. Interestingly, when studying the effect of water in two ether-functionalized imidazolium ILs on cyclic voltammetry measurements using a platinum electrode, Migliorini et al.[133] observed the diminished cathodic currents in [Me(OCH_2CH_2)_3-MIM][CH_3SO_3] with as little as 0.19 mM of water, and extremely reduced charge transfer processes (for both cathodic and anodic) in [MeOCH_2CH_2-MIM][CH_3SO_3] containing 0.19–1.1 mM water. It was suspected that a new species was produced between the imidazolium ILs and water, which blocked the active sites of the platinum electrocatalyst. Despite its unknown identity, this species was speculated to be formed by the hydrolysis of the imidazolium cation with the release of protons. Measurements of pH confirmed the increase of proton concentration in these ILs with the addition of water.

Yeon et al.[48] reported that some hydroxyl-functionalized imidazolium and morphorinium ILs (paired with BF_4^−, PF_6^− or Tf_2N^−) also have some superb electrochemical properties: [HOCH_2CH_2-MIM]^+ type ILs have wide electrochemical windows in the range of 5.4–6.4 V and ionic conductivities ranging from 2.1–4.6 mS/cm at 25 °C; hydroxyl-functionalized morpholinium ILs have large electrochemical windows (5.2–6.2 V) as well but much poorer conductivities (0.00066–0.087 mS/cm at 25 °C) due to the high viscosities of these liquids. Pinkert et al.[105] reported that hydroxyl-containing protic ammonium ILs of acetate or formate have conductivity values ranging from 4.8×10^{-4} to 2.3 S/m at 5–75 °C, which suggests that their Walden products (molar conductivity × viscosity) are comparable to aprotic ILs. Interestingly, Wu et al.[79] indicated that hydroxyl-functionalized pyrrolidinium and piperidinium ILs (with Tf_2N^− as anions) exhibit wider potential windows than those of corresponding ether-functionalized ILs.

3.5 Polarity, hydrophilicity, and H-bonding capability

Although Coulomb force is the dominating interaction between ions in ILs, hydrogen bonding can have a considerable impact not only on the IL structure, but also on properties such as melting points, viscosities, and enthalpies of vaporization,[134] as well as IL interactions with solute molecules. Dzyuba and Bartsch[135] reported a higher solvent polarity for ether-/hydroxyl-functionalized imidazolium ILs than those of non-functionalized ILs based on optical measurements with solvatochromic dyes (*i.e.*, Reichardt's dye and Nile Red). Similarly, using solvatochromic measurements of Nile Red, Jin et al.[91] observed hydroxyl-containing ILs to have higher values of π_{NR} (1.24–1.55) than alkyl-substituted ILs (1.01 ± 0.05) ($\pi_{NR} = 0$ for cyclohexane, and 1.00 for DMSO), which indicates the former ILs have higher solvent polarities due to the presence of hydroxyl groups. Using fluorescence measurements of pyrene and pyrene-1-carboxaldehyde, the polarity of an ammonium IL grafted with two PEG-350 methyl ether chains was determined to be between that of methanol and acetonitrile.[59] Chiappe et al.[136] carried out a solvatochromic study on a

variety of hydroxyl-functionalized ILs confirming that the introduction of –OH groups on the cation increases polarity, and the impact of the first –OH group is more pronounced than subsequent ones. The Welton group[137] suggest that hydroxylcontaining ILs have a higher hydrogen-bond acidity (the α value based on the Kamlet-Taft scale) than non-functionalized ILs.

The static relative dielectric permittivity, ε, (also known as the static dielectric constant) of a solvent is a relative measure of its polarity. The Weingartner group[138] determined the ε values of 42 ILs at 25 °C using dielectric relaxation spectroscopy. Interestingly, but not surprisingly, hydroxyl-containing ILs exhibited higher dielectric constants than nonfunctionalized ILs. For example, $[EtNH_3][NO_3]$ and $[EtNH_3][HCOO]$ have ε values of 26.3 and 31.5, respectively, whereas $[(HO)EtNH_3][NO_3]$, $[(HO)EtNH_3][HCOO]$ and $[(HO)EtNH_3][OAc]$ have much higher values of 60.9, 61.0, and 58.3, respectively. $[(HO)EtNH_3][lactate]$ has an even a higher ε value of 85.6. However, multiple hydroxyl groups on ILs cause a decrease in the dielectric constant (*i.e.*, $\varepsilon = 31.0$ for $[(HOEt)_3NH]$ [OAc] and $\varepsilon = 59.7$ for $[(HOEt)_3NH][lactate]$). Hydroxyl-functionalized imidazolium or pyridinium ILs have lower ε values (23–35) than protic ammonium salts.

The addition of hydroxyl or alkoxy group to the cation remarkably increases the hydrophilicity of ILs. For example, 1-(2-hydroxypropyl)-3-methylimidazolium based ILs (paired with various anions such as Cl^-, NO_3^-, PF_6^- and Tf_2N^-) are more hygroscopic and more miscible with water than the alkyl-substituted analogues.[75] Schrekker et al.[139] observed that the incorporation of an ether chain into the imidazolium cation greatly improves hydrophilicity and water miscibility of PF_6^- based ILs; the hydrophilicity increases in the order of $[BMIM][PF_6] < [MeO(CH_2)_2\text{-}MIM][PF_6] < [Me(OCH_2CH_2)_3\text{-}MIM][PF_6]$, and at 50 °C the latter is completely miscible with water. A dimethylammonium-based IL containing two PEG-350 methyl ether chains is completely miscible with water due to the hydrophilic nature of the two long alkoxy chains[59] while 1-(2-hydroxyethyl)-3-methylimidazolium hexafluorophosphate $([(HOCH_2CH_2)\text{-}MIM][PF_6])$, is soluble in water at >50 kg m^{-3} at 25 °C.[140] Deng et al.[141] observed that the octanol-water partition coefficients decrease as the side chain of imidazolium cations are functionalized with ether and ester groups, indicating a reduced IL lipophilicity. Leicunaite et al.[53] compared the elution sequence of several oxygen-functionalized ILs by HPLC analysis using mixed-mode reversed-phase/cation exchange stationary phase and aqueous acetonitrile gradient mobile phase, suggesting the decreasing order of IL hydrophilicity as: $[HO(CH_2)_2\text{-}MIM]Cl > [HO(CH_2)_2(OCH_2CH_2)_2\text{-}MIM]Cl > [CH_3O(CH_2)_2\text{-}MIM]Cl > [CH_3(OCH_2CH_2)_2\text{-}MIM]Cl > [CH_3CH_2O(CH_2)_2\text{-}MIM]Cl > [CH_2=CHO(CH_2)_2\text{-}MIM]Cl > [CH_3(OCH_2CH_2)_3\text{-}MIM]Cl > [PhO(CH_2)_2\text{-}MIM]Cl$

Imidazolium ILs form an extended hydrogen-bonded network in both solid and liquid states, with a main contributor being the C-2 hydrogen of the imidazolium ring.[142, 143] The strength of these H-bonds is more dependent on the type of anions than the oxygen-functionalization of side chain[34] even though multiple oxygen atoms in the IL side chain can serve as H-bond acceptors for solute molecules. Nevertheless, X-ray crystallography and IR spectroscopy have confirmed that short chain ether groups are involved in intermolecular hydrogen bonds (C-H···O contacts, Scheme 10).[125] The ether chains compete with anions for cations interaction; as a result, the cation–anion interaction is reduced resulting in the formation of cation dimers in ether-functionalized ILs.[101, 125] Lovelock et al.[144] deployed angle resolved X-ray photoelectron spectroscopy (ARXPS) to study the surface composition of alkyl-substituted and ether-grafted imidazolium ILs, observing the enrichment of aliphatic carbons at the surface for longer alkyl chains ($n \geq 4$) with no such enrichment for ether-functionalized ILs. It was postulated that the H-bonding interactions between ether chain oxygen atoms and hydrogen atoms on the imidazolium ring cause an increase in the lattice

energy in the bulk of IL. For this reason, the termination of the surface with the ether-functionalized chain is energetically unfavorable, resulting in an outer surface composed of the non-coordinating CF_3 groups of the anions. Ficke and Brennecke[145] suggest that appending a hydroxyl group to the ethyl chain of the $[EMIM]^+$ cation (becoming $[(HO)EMIM]^+$) increases the cation–anion H-bonding and IL–IL interactions from the large positive charge on the hydrogen atom in the –OH group. The interaction between the –OH and the anion is preferentially stronger than the H-bonding between –OH and water, resulting in a less negative excess enthalpy for $[(HO)EMIM][CF_3COO]$/water mixtures than for $[EMIM][CF_3COO]$/water. Similarly, a reduction in cation–anion interactions was observed in carboxyl-functionalized ILs, which is attributed to the strong O-H···O interaction between two carboxyl groups of two participating cations.[146] Kempter and Kirchner[147] provided an in-depth discussion about H-bonding in functionalized and non-functionalized ILs from both experimental and theoretical aspects. The Anderson group[148, 149] derived the solvation properties of functionalized ILs using a solvation parameter model and suggest that appending a hydroxyl moiety to the IL cation greatly increases its H-bond acidity with a small increase in H-bond basicity and no change in dipolarity. They also confirmed a slight increase in the H-bond basicity in the presence of ether functionality on the cations. The H-bonds formed in these functionalized ILs may prove crucial to the stability and activity of biomolecules in oxygen-functionalized ILs (see section 4.9 below).

Recent studies on the mixtures of glycols and regular ILs offer some valuable insights into the interaction between glycol chains and ILs. Patrascu et al.[150] observed the formation of micelles when dissolving nonionic surfactant alkyl PEG-ethers in [BMIM]X (X = BF_4^-, PF_6^- and Tf_2N^-). The Inoue group[151, 152] further examined the interactions between PEG-type nonionic surfactants as solutes and IL molecules ($[BMIM][PF_6]$ or $[BMIM][BF_4]$) as solvents through measuring the cloud point temperatures and ^1H NMR chemical shifts. Their results suggest that oxygen atoms in the PEG chains may act as H-bond acceptors toward the cations (in particular, with C-2 hydrogen of the imidazolium ring) in competition with IL anions. The cloud point temperature increases with the length of the surfactant PEG chain, indicating a longer PEG chain attributes a higher hydrophilicity of surfactants. As PF_6^- has a weaker H-bond basicity than BF_4,[109] the interaction between the cation and the PEG chain is stronger in $[BMIM][PF_6]$ than in $[BMIM][BF_4]$. As a result, the surfactant molecules are more solvophilic in $[BMIM][PF_6]$ than in $[BMIM][BF_4]$. Sarkar et al.[153] studied the polarity of a binary mixture comprising $[BMIM][PF_6]$ and tetra(ethylene glycol), and observed unusual hyperpolarity [E_T, a, π^* values that exceed the pure component values]. This phenomenon is explained by FT-IR measurements, which suggests H-bonding between $BMIM^+$ and PEG oxygen atoms, and between PF_6^- anion and the terminal –OH PEG groups. Similarly, Trivedi and Pandey[154] reported hyperviscosity when mixing $[BMIM][PF_6]$ with PEG-600 or PEG-1000, but not with PEG-200 and PEG-400. The hyperviscosity was rationalized by the stronger H-bonding between IL and PEG in former two mixtures compensating the losses in Coulombic attraction and van der Waals interactions due to the addition of PEG. Chaurasia et al.[155] prepared polymer electrolyte films from PEG (MW = 6×10^5) and 1-ethyl-3-methylimidazolium tosylate and confirmed the complexation between the cation and the ether oxygen by FT-IR/DSC/XRD characterization methods, although the specific interactions involved were not identified. Singh et al.[156] studied the interactions between several ILs and ethylene glycol (EG) using steady–state and time–resolved fluorescence, FT-IR, and NMR spectroscopy. They found that the oxygen's lone-pair electrons and hydroxyl protons of EG interact strongly with the aromatic ring protons and $[OctSO_4]^-$, respectively, in the EG–$[BMIM][OctSO_4]$ system; however, in EG-$[BMIM][BF_4]$ and EG-$[OMIM][BF_4]$ systems, the interaction between the hydroxyl protons of EG and the anion (BF_4^-) is weaker than that between oxygen's lone-pair electrons and aromatic ring protons. They also concluded that multiple H-bonding

interactions existing in these systems at the microscopic level are not necessarily revealed in the mixing macroscopic behavior. Forte et al.[157] measured the liquid–liquid equilibria (LLE) data of 20 binary mixtures consisting of imidazolium ILs (with anions of dca$^-$ and Tf$_2$N$^-$) and glycols, glycerol, or 1-butanol. A complete miscibility was observed for the hydrophilic dca$^-$-based ILs and polyhydroxy alcohols, but a limited solubility was found for Tf$_2$N$^-$-based ILs in butanediols. Wu et al.[158] investigated physical properties of a binary mixture of 1-methyl-3-pentyl-imidazolium hexafluorophosphate and PEG-200, and observed the excess molar volumes, excess volume expansivity, and viscosity all have negative deviations from the ideal solution, but the refractive index exhibits a positive deviation value over the whole composition range. In addition, excess molar volumes and excess volume expansivity are more negative at higher temperatures, while viscosity deviations are less negative at higher temperatures.

3.6 Other properties

Other physicochemical properties (such as activity coefficients at infinite dilution, Hildebrand solubility parameters, surface tension, contact angle, and wetting film stability) of pure and mixtures of oxygen-grafted ILs can be found in the literature for hydroxyl ammoniums,[105, 159–164] including choline-based ILs,[165–170] hydroxyl imidazoliums,[103, 171–174] hydroxyl pyridiniums,[175–178] ether-functionalized ammoniums,[179] and ether-functionalized imidazolium based ILs.[180]

4. Applications of Ether- and Hydroxyl-Functionalized ILs

4.1 Electrolytes in electrochemistry

Since the early 1980s, ether-functionalized ILs were synthesized and investigated as alternative ambient-temperature electrolytes, such as methoxyethyl ethyl dimethylammonium tetrafluoroborate ([CH$_3$OCH$_2$CH$_2$-Et-Me$_2$N][BF$_4$], T_m = 13 °C and T_g = −98 °C),[181] and methoxymethyl ethyl dimethylammonium tetrafluoroborate ([CH$_3$OCH$_2$-Et-Me$_2$N][BF$_4$], T_m = −16 °C and T_g = −115 °C).[182] In the 1990s, much attention was focused on the incorporation of cationic or anionic units on PEGs to produce the liquid state of the ion conductive polymers (cation-tethered PEG, anion-tethered PEG, or their mixtures), and many of these studies have been reviewed elsewhere.[13, 23] As a typical illustration of this concept, the Ohno group[22, 56] grafted sulfonamide, ethylimidazolium or sulfonate groups to the ends of PEG oligomers (MW ranging from 150–2,000) resulting in viscous liquids (Scheme 11). However, their mixtures exhibited drastically decreased T_g and increased ionic conductivity. For example, for PEG-150 with sulfonamide groups, T_g decreased from 3.2 °C to −61.6 °C and its ionic conductivity increased about 10^5 times to 0.0612 mS/cm at 50 °C after mixing with PEG-150 with appended ethylimidazolium groups. Similarly, Dickinson et al.[66] described the preparation of viscous molten salts containing either polyether-tailed 2-sulfobenzoate or polyether-tailed triethylammonium as counterions of ruthenium hexamine, metal trisbipyridines, metal trisphenanthrolines and ionic forms of aluminum quinolate, anthraquinone, phthalocyanine, and porphyrins and measured their ionic conductivities and cyclic voltammetry behavior. The most obvious application of oxygen-functionalized ILs is as electrolytes for lithium batteries due to their low viscosities, high conductivities, and reasonably high electrochemical stability.[45, 50, 84, 85, 183] In particular, ether-functionalized ILs have shown their unique roles as electrolytes in electric double layer capacitors (EDLCs) and dye-sensitized photoelectrochemical solar cells (DSSC).

Electric double layer capacitors (EDLCs) do not rely on chemical reactions for charging and discharging electricity as do rechargeable batteries, but physically store energy *via* the electric double layer. Generally, EDLCs have a longer life time and higher power density

than rechargeable batteries. In addition to their high performance, EDLCs are environmentally benign devices as heavy metal materials are not a necessity. The purpose of using ILs in EDLCs is to further improve their energy density and high-temperature stability. Sato et al.[89] found that an ether-grafted IL, [$CH_3OCH_2CH_2$-Me-Et_2N][BF_4], has a wide potential window (6.0 V) and a high ionic conductivity (4.8 mS cm^{-1} at 25 °C). Subsequently, an EDLC was constructed by a pair of activated carbon electrodes with this IL as the electrolyte. At a working voltage of ~2.5 V, the EDLC exhibited a higher capacity above room temperature and a better charge–discharge cycle durability at 100 °C than a conventional EDLC using an organic liquid electrolyte such as [Et_4N][BF_4] in propylene carbonate. Higashiya et al.[184] prepared oxygen-containing spirobipyrrolidinium salts (Scheme 12) for potential applications as electrolytes in EDLCs. This group observed that introducing an oxygen atom (and alkyl groups to break the symmetry) to the spirobipyrrolidinium ring led to a reduction in melting points and viscosities of the resulting ILs. Meanwhile, these new salts maintained a high electrochemical stability: the potential window ranged from 5.9 to 7.3 V (0.65 M in acetonitrile), and the conductivity (2.0 M in acetonitrile) varied from 48–55 mS cm^{-1}.

Pandey et al.[185] designed new EDLC cells by using multiwalled carbon nanotube (MWCNT) electrodes and polymer electrolyte films comprising of PEG (MW ~ 6×10^5), Li(OTf) or Mg(OTf)$_2$, and [EMIM][OTf]. Although PEG chains were not covalently attached to the IL cation, the polymer electrolytes exhibited ionic conductivities of ~0.1 mS/cm at room temperature and the electrochemical stability window of ~4 V. These new EDLC cells with Mg-and Li-based polymer electrolytes exhibited specific capacitance values of 2.6–3.0 and 1.7–2.1 F/(g of MWCNT) respectively, and the Mg-based polymer electrolyte performed slightly better than the Li-type.

An ether-functionalized IL, 3-[2-(2-methoxyethoxy)ethyl]-1-methyl-imidazolium iodide, was used as the liquid electrolyte in a DSSC. However, the efficiency of liquid electrolyte was found inferior to those of sol–gel electrolytes.[186] The Lin group[32] attached different PEG methyl ether chains (PEG-150, 350, 550 and 750) to 1-methylimidazole to form ILs as electrolytes for DSSCs. They found that a longer PEG chain resulted in an increased apparent diffusion coefficient of triiodide, an improved dye regeneration rate, lower charge transfer resistance of triiodide reduction, and a higher ionic conductivity despite the higher solvent viscosity. Yang et al.[187] used PEG-1000 functionalized 1-methylimidazolium and ether-functionalized iodide mixed with 1-alkyl-3-methylimidazolium iodides as electrolytes for DSSCs. These new electrolytes showed high ionic conductivities and a large apparent diffusion coefficient for triiodide, particularly with the further addition of *N*-methylimidazole.

KCl-type salt bridges have limited uses for samples with low ionic strength, however, newer salt bridges constructed from hydrophobic ILs are capable of overcoming this restriction.[188] Specifically, an ether-functionalized phosphonium IL, tributyl(2-methoxyethyl)phosphonium bis(pentafluoroethanesulfonyl)amide, exhibited stable liquid junction potentials when in contact with aqueous solutions with low ionic strength (as low as 1 μM), and thus is a foreseeable electrolyte for salt bridges in accurate determination of pH and other single ion activities.[42] In addition, this IL has a low solubility in water (0.2 mM at room temperature) and is more chemically stable in alkaline solutions than tetraalkylphosphonium salts.

4.2 Extraction, Biphasic System

Revelli et al.[189] studied the activity coefficients of 52 organic compounds in four functionalized ILs ([MeO-MeO-IM][Tf$_2$N], [MeO(CH$_2$)$_2$-MIM][Tf$_2$N], [HO(CH$_2$)$_2$-MIM] [Tf$_2$N], and [NC-(CH$_2$)$_3$-MIM][dca]) using inverse gas chromatography. This group[189, 190]

further advocated the potential of dicyanamide (dca⁻)-based ILs for liquid-liquid extraction of volatile organic substances from aliphatic mixtures due to the high selectivity of these polar functionalized ILs; however, Tf_2N^--based ILs surprisingly exhibited about the same selectivity as common organic solvents. The Kragl group[191] discovered that an IL within the Ammoeng family (Ammoeng 110, Scheme 13) proved quite effective in forming an aqueous two-phase system for the purification of alcohol dehydrogenases; the IL is capable of stabilizing the enzymes and enhancing the solubility of hydrophobic substrates.

4.3 CO_2 capture and gas separation

4.3.1 Gas solubility and CO_2 capture—Due to the high potential of ILs being alternative media for capturing acid gases (such as CO_2, H_2S and SO_2), the gas-liquid equilibrium data in ILs are fundamentally important. General reviews on gas solubility and CO_2 capture in ILs can be found in the recent literature.[192–194] The He group[195] has summarized the latest progress on CO_2 absorption and chemical conversion of CO_2 by using TSILs including amino-functionalized, hydroxyl-functionalized and protic ILs. Meanwhile, intrinsic drawbacks such as extensive energy consumption for CO_2 desorption, low capture efficiency and slow sorption kinetics were also addressed. This section is devoted to the gas solubility and separation in ether-/hydroxyl-functionalized ILs.

The solubility and selectivity of gases are dependent on the chemical structures of IL cations and anions. The Henni group[196] used the COSMO-RS method, an excess Gibbs energy model for liquid mixtures based on surface charge interaction, to predict Henry's Law constants of CO_2, CH_4 and N_2, as well as the selectivity for CO_2/CH_4 and CO_2/N_2 separation as a function of temperature in 2,701 ILs from the BP-COSMO-IL database comprising 73 cations and 37 anions. Overall, CO_2 was more soluble in ILs than methane and nitrogen; this high CO_2 solubility is crucial to the solvent selection for CO_2 capture. Generally, a higher CO_2 solubility was observed for ILs carrying fluorine-containing anions than acetate, borate, sulphate, or halogenide based ILs. For the same anion, the solubility is usually higher in guanidium, isouronium and pyrrolidinium cation containing ILs. Interestingly, it was shown that ether- and hydroxyl-functionalized cations actually decreased the CO_2 solubility while the anions functionalized with these groups (such as $[MeOEtSO_4]^-$ and [lactate]⁻) increased the CO_2 solubility. The Aparicio group[197] suggests that hydroxylammonium-based ILs, 2-hydroxyethyl-trimethylammonium L-(+)-lactate and tris(2-hydroxyethyl)methylammonium methylsulfate, have low CO_2 absorption capability based on COSMO computational prediction. However, experimental studies of the effect of oxygen-functionalization on CO_2 solubility seem far more complicated.

Ether-functionalization: It is suggested that the ether oxygen atoms (Lewis base) interacts with the CO_2 carbon atom (Lewis acid) forming a 1:1 van der Waals complex.[198] Oligo(ethylene glycol) functionalized imidazolium ILs were reported to be capable of dissolving similar amounts of CO_2 as alkyl-substituted analogues while dissolving less N_2 and CH_4. As a result, the ideal solubility selectivities of CO_2/N_2 and CO_2/CH_4 were improved by 30–75% by these ether-grafted ILs.[70] This represents an advancement of using alternative solvents for bulk fluid CO_2 separations in gas separation technology. Muldoon et al.[199] determined the CO_2 solubility under low and high pressures in a range of ILs including fluorinated ILs and nonfluorinated ILs possessing structures likely to increase the solubility of CO_2. The IL anion also plays a critical role in CO_2 solubility.[200] Although fluorinated ILs can dissolve more CO_2, their use raises some environmental concerns due to their poor biodegradability. On the other hand, non-fluorinated ILs containing long alkyl chains with branching or ether groups (such as Ecoeng 500, Scheme 14) have showed a high affinity for CO_2 (comparable to $[HMIM][Tf_2N]$ at all pressures). Sharma et al.[201] indicated that ether-functionalized imidazolium ILs ($[CH_3OCH_2-MIM]X$) have a high absorption

capability for CO_2, reaching *ca.* 0.9 mol CO_2 per mol of IL at 30 °C; the CO_2 absorption capability increases with anions in the order of $BF_4^- < dca^- \sim PF_6^- \sim OTf^- < Tf_2N^-$. They further suggested the absorption of CO_2 in ether-functionalized ILs was a chemical process based on FT-IR and ^{13}C NMR spectra, where one CO_2 molecule reacts with one IL molecule to form carbamic acid. On the contrary, the Gomes group[202] observed the solubilities of CO_2, methane and ethane in ester or ester and ether-functionalized imidazolium ILs are on the same order of magnitude as in alkylimidazolium ILs; the extra functionality exhibited a minimum impact on the solvation ability of ILs. A further molecular simulation[203] indicates the inclusion of ester groups on cations can modify the relative size of polar and nonpolar domains in ILs, but imposes no significant impact on the solvation of gases (such as CO_2).

Hydroxyl-functionalization: Wang et al.[204] developed a robust chemisorption system consisting of equimolar hydroxyl-functionalized ILs and superbases for CO_2 capture under atmospheric pressure. This system has exhibited several advantages such as (a) fast and reversible capture of about one mole of CO_2 per mole of superbase; (b) easy release of captured CO_2 by mild heating or purging with an inert gas, and (c) a recyclable system with minimal loss of activity.

The gas-liquid equilibria of binary mixtures consisting of CO_2 + *N*-methyl-2-hydroxyethylammonium-based ILs [*i.e.*, *N*-methyl-2-hydroxyethylammonium acetate (m-2-HEAA) and *N*-methyl-2-hydroxyethylammonium formate (m-2-HEAF)] were measured by the Mattedi's group[205] in the temperature range of 293–353 K and at pressures up to 80 MPa; no specific interaction was observed between CO_2 and m-2-HEAF, but m-2-HEAA was found to interact with CO_2 molecules chemically at low gas molar concentrations; a further study of a ternary mixture of CO_2 + CH_4 + m-2-HEAA suggests that this IL could be used to selectively separate CO_2 from a methane mixture. The Zhang group[206] synthesized a series of hydroxyl ammonium ILs and measured the solubilities of CO_2 in these ILs at temperatures ranging from 303 to 323 K and pressures ranging from 0 to 11 MPa. The highest CO_2 solubility in tri(2-hydroxyethyl)-ammonium lactate is higher than that in [EMIM][EtSO$_4$] but lower than those in [BMIM][PF$_6$] and [OMIM][PF$_6$]. Compared to aqueous amines used in industry, these ammonium-based ILs have limited solubilities for CO_2. The Jalili group[207, 208] measured the solubility of CO_2 in a series of 1-(2-hydroxyethyl)-3-methylimidazolium ([hemim]$^+$) based ILs carrying different anions (PF$_6^-$, OTf$^-$ and Tf$_2$N$^-$) at temperatures between 303.15 and 353.15 K and pressures up to 1.3 MPa. The anion effect on the CO_2 solubility is in a decreasing order of $Tf_2N^- > OTf^- > PF_6^- > BF_4^-$. It was also found that the CO_2 solubility in these hydroxyl-grafted ILs was greater than corresponding [EMIM]$^+$ type of ILs containing the same anions, advocating the high potential of these functionalized ILs for CO_2 capture. However, the Gomes group[104] suggests that the presence of hydroxyl or ester groups in ammonium ILs has no impact on CO_2 solubility, but functionalized pyridinium ILs dissolve much less CO_2 (up to a 48 % decrease in mole fraction); this is explained due to an unfavorable entropic contribution to the Gibbs energy of solvation.

The Xiong group[209] prepared imidazolium-based ILs with symmetrical ester or hydroxyl groups, and further synthesized their corresponding polymers through melt condensation polymerization. The resulting poly(ionic liquid)s (PILs) were studied as CO_2 absorbers along with IL monomers at 25 °C under a low pressure (648.4 mmHg) using a thermogravimetric analyzer. Their results identified 1,3-di(2-hydroxylethyl)imidazolium hexafluorophosphate having the highest CO_2 absorption capacity (10 mol %) among those of PILs and ILs studied, which was believed to be better than previously reported ILs.

Reversible chemical absorption of CO_2 using aqueous alkanolamines (R_1R_2NROH) forms bicarbonate and carbamate ions *via* reactions shown in Scheme 15 with monoethanolamine ($HOC_2H_4NH_2$, MEA) as an example.[210] where $MEACO_2^-$ represents the carbamate ion $HOC_2H_4NHCOO^-$, and $MEAH^+$ ($HOC_2H_4NH_3^+$) represents the protonated MEA. However, this aqueous system suffers from a high demand for energy consumption and the loss of water and MEA by evaporation during the thermal regeneration cycle. Therefore, Huang et al.[211] suggested a simple route for thermally stable enrichment of CO_2 captured by monoethanolamine ($HOC_2H_5NH_2$, MEA) in hydroxyl-functionalized imidazolium-based ILs with the aid of strong H-bonding between protonated monoethanolamine and the chloride ion. The interaction between $MEAH^+$ and Cl^- stabilizes $MEAH^+$ and discourages $MEAH^+$ from combining with $MEACO_2^-$ [reverse reaction (3)], and consequently increases the capacity and stability of the captured CO_2. The equilibrium constant for reaction (3) in MEA–[C$_3$OHmim]Cl was about 66 % larger than that in MEA–[C$_3$OHmim][BF$_4$].

4.3.2 Gas separation and SO$_2$ absorption—Bara et al.[69] polymerized dicationic RTILs containing ether (or alkyl) chains (Scheme 16), and used the resulting thin films as membranes for permeability tests of gases (CO_2, N_2, CH_4, and H_2). Due to the highly restricted diffusion through the membrane, the gas permeabilities were significantly lower than other poly(RTIL) membranes. As the CH_4 and N_2 fluxes were so small, the membrane could act as the barrier layer for these gases.

Another important application of these functionalized ILs is their use as SO_2 absorbents. Yuan et al.[212] studied the solubility of SO_2 in hydroxyl-functionalized ammonium ILs, and reported the solubility of SO_2 decreasing in the order of 2-hydroxyethylammonium > tri(2-hydroxyethyl)ammonium > 2-(2-hydroxyethoxy)ammonium (for cations), and lactate > acetate > formate (for anions). Thus, 2-hydroxyethylammonium lactate exhibited the highest absorption capacity for SO_2 with an equilibrium concentration of SO_2 of 0.5107 (mole fraction). Zhai et al.[213] prepared a number of hydroxyl ammonium ILs carrying different anions (lactate, acetate and formate), and proposed these ILs could absorb SO_2 from flue gas (Scheme 17). Ethanolamine lactate was capable of dissolving 0.51 mole fraction of SO_2 despite the high viscosity of this IL. Hong et al.[62] prepared a series of ether-functionalized imidazolium methanesulfonates, and found these ILs could dissolve at least 2 moles of SO_2 molecules per mol of IL at 30 °C and atmospheric pressure. They also observed that the SO_2 solubility in ILs increases not only with the pressure, but also with the increasing number of ether oxygen atoms. A further study of FTIR spectroscopy and quantum mechanical calculation suggests the high SO_2 solubility can be attributed to several interactions of SO_2 with methanesulfonate anion, ether oxygen atoms, and atoms on the imidazolium ring. Their study also demonstrated that the absorbed SO_2 in ILs could be easily desorbed by heating the mixture at 100 °C under N_2 flow.

Cui et al.[214] prepared ether-functionalized phosphonium and imidazolium ILs carrying tetrazolate anions, and found these ILs could absorb more SO_2 (4.43–5.0 moles per mole of IL at 20 °C and 1 bar) than non-functionalized analogues (3.37–4.0 moles). The functionalization of both cations and anions leads to the efficient SO_2 capture through a combination of chemical and physical absorption.

In summary, ether/hydroxyl-functionalized ILs have high potentials for industrial applications in CO_2 capture, gas separation, and SO_2 absorption based on the structure-property relationship of these ILs. However, the effect of functionalization on the physicochemical properties of ILs deserves a further study in order to design new affordable ILs with high capacity, high biodegradability, and low toxicity for these applications.

4.4 Carbohydrate dissolution

In 2001, Kimizuka and Nakashima[215] prepared two ether-functionalized ILs, namely,1-methoxymethyl-3-methylimidazolium bromide ([MeOMe-MIM]Br) and 1-methoxyethyl-3-methylimidazolium bromide ([MeOEt-MIM]Br), and found they were capable of dissolving carbohydrates (such as β-D-glucose, α-cyclodextrin, amylose and agarose) and a glycosylated protein (glucose oxidase); interestingly, they also observed the formation of stable bilayer membranes when glycolipids were dispersed in these ILs; in addition, self-assembling ionogels were formed by the gelation of ILs after dissolving amide group enriched glycolipids in them. Park and Kazlauskas[216] observed the solubility of D-glucose in [MeOEt-MIM][BF$_4$] was about 5 mg mL^{-1} at 55 °C.

The Sheldon group[30] reported high solubilities of D-glucose (66–91 g L^{-1} at 25 °C) and sucrose (50–249 g L^{-1} at 25 °C) in short-ether-chain-grafted imidazolium ILs containing dca$^-$ anions. However, they also pointed out the high sugar solubility was not due to the oxygenated side-chain, but due to the high H-bond basicity of dca$^-$.[217] The Zhao group[67, 218, 219] developed a series of new acetate-based ILs containing cations functionalized with glycol monoether chains (Scheme 18). These new ionic media have exhibited remarkable solubilities for a variety of substrates, including up to 1.1–5.3 M D-glucose (at 60 °C), 10–12 wt% cellulose (at 110 °C), 6–15 wt% xylan (at 110 °C), >13–22 wt% lignin (at 110 °C), 200–420 mM 3,4-dihydroxy-DL-phenylalanine (at 20 °C), and up to 640 mM betulinic acid (at 25 °C). Those hydroxyl-containing and/or protic ILs are recognized less likely to dissolve cellulose because of their H-bond donating nature. The H-bond basicity of the anion (acetate) is a major factor for dissolving these substances; however, the ether-functionality also plays several important roles: (1) reducing the melting points of ILs, (2) reducing the viscosities of ILs, (3) adjusting the polarity and hydrophobicity of ILs to be more compatible with solute molecules. More recently, Chen et al.[86] observed that dialkoxy-grafted quaternary ammonium ILs carrying acetate anions could dissolve 13–18 wt% microcrystalline cellulose (DP 215–240) at 80 °C. More interestingly, Zhang et al.[220] reported that mixtures of cholinium acetate with 10–15 wt% alkylammonium salt (such as tributylmethylammonium chloride, triethylmethylammonium chloride or tributylbenzylammonium chloride) were capable of 5–6 wt% microcrystalline cellulose at 110 °C, potentially offering less expensive solvents for cellulosic biomass pretreatment. Liu et al.[221] prepared a series of cholinium ILs with amino acid anions capable of dissolving up to 14–22 wt% lignin, up to 8.5% xylan, but little cellulose; they also observed faster enzymatic hydrolysis of microcrystalline cellulose and rice straw after pretreatment with [cholinium][Glycinate]. Bose et al.[222] observed that tris-(2-hydroxyethyl)-methylammonium methylsulfate was only able to dissolve 1% (w/w) cellulose, but this IL appeared to be more compatible with *Aspergillus niger* endo-1,4-β-*D*-glucanase (a cellulase component) than [BMIM]Cl and [BMIM][MeSO$_4$]. Ohira et al.[223] found that *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium ILs carrying amino acid anions (such as alaninate) could dissolve up to 5–12 wt% cellulose at 100 °C; their results further indicated that cellulose was transformed from Type I to Type II by the IL pretreatment, which greatly improved the enzymatic hydrolysis rate of cellulose. A more comprehensive overview of ILs for dissolving carbohydrates can be found in a recent review.[224]

Since conventional organic solvents are not always effective in dissolving polar carbohydrate molecules, their high solubilities in ILs enable numerous opportunities for carbohydrate chemistry such as chemical/enzymatic conversions of sugars,[67, 218] and pretreatment of lignocelluloses for bioethanol production.[219, 225226]

4.5 Dissolution of inorganic salts and polymers

Branco et al.[26] report that ether- or hydroxyl-functionalized ILs dissolve 3–11 times more $HgCl_2$ and 3–16 times more $LaCl_3$ than alkyl-substituted ILs, although the solubility of LiCl is not generally affected by the oxygen functionality. They also concluded that BF_4^- based ILs are better solvents for $HgCl_2$ and $LaCl_3$ than PF_6^- type ILs, and the solubility of these two salts also increases with the increasing cations chain length. They argued that the solubility trend could be extrapolated to alkaline, transition metals and lanthanides salts.

Holbrey et al.[227] prepared a hydrophobic dicationic IL containing a short ethylene glycol spacer in the cation (see Scheme 19), and found that the ether linkage imparts a high degree of flexibility and hydrophilicity. A single crystal X-ray diffraction study suggests a strong intermolecular cation–cation H-bond between C(2)-H of the imidazolium ring with the ether oxygen of the second cation. The ether-functionality greatly improved the distribution ratio of Hg^{2+} (as high as 54) between the IL and aqueous solution when compared with that of an alkyl-substituted IL (<1), however, such an improvement was not observed for Cs^+. A possible carbene extraction mechanism was proposed for the high distribution of Hg^{2+} in the IL.

2-Hydroxyethylammonium formate (HEAF) was prepared with a freezing point of − 82 °C, a viscosity of 105 mPa s at 25 °C, and a conductivity of 3.3 mS cm^{-1} at 25 °C.[228] Despite its low thermal stability (150 °C), this inexpensive IL was found capable of dissolving inorganic salts (8–28 g/mL) and some polymers (polyaniline and polyprrrole). Based on the conductivity measurements, an interesting observation was reported: salts of weak bases (such as NH_4Cl and [Et_3NH]Cl) dissociate into individual ions in HEAF, while strong electrolytes (such as NaCl and Na_2SO_4) do not appear to dissociate in HEAF.

A hydroxyl-containing IL, 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride, was reported to have a high conductivity (2.3 mS/cm at room temperature) and a high thermal stability (up to 230 °C), and could dissolve 20–35 wt% inorganic salts (such as NaCl and NH_4Cl) at 25 °C as well as 10 wt% pulp cellulose at 80 °C.[171] The two protic ILs, *N*-(2-hydroxyethyl)ammonium formate (HEAF) and *N*-(2-hydroxyethyl)ammonium acetate (HEAA), were illustrated to be capable of dissolving up to 70 % zein, a natural but water-insoluble protein from corn processing.[229] This offers an alternative technology for a low cost and environmentally benign zein processing.

4.6 Antimicrobial and antielectrostatic activities

An excellent antielectrostatic effect was observed by the Pernak group[25] in 3-alkoxymethyl-1-methylimidazolium tetrafluoroborates with 8–11 carbon atoms in the alkoxymethyl group, which is similar to that of the known antistatic agent Catanac 609. The same group[36] also prepared 1-alkoxymethyl-3-substituted-pyridinium chlorides with alkoxy chain length from 3–18 carbons, and found the antielectrostatic effect and antimicrobial activities were affected by the type of substituent at the 3-position in the pyridine ring and by the alkoxy chain length at the 1-position. In particular, 1-dodecyloxymethyl-3-dimethylaminopyridinium chloride showed strong antimicrobial activities, which are comparable to benzalkonium chloride. In addition, 1-alkoxymethyl-3-hydroxypyridinium chlorides exhibited antielectrostatic properties, but not antimicrobial activity.[36]

The Pernak group observed higher antimicrobial activities against cocci, rods, and fungi for alkoxymethyl-substituted pyridinium salts,[230] imidazolium ILs[231] (with BF_4^- or PF_6^- as anions), and choline-derived ammonium ILs (with acesulfamate anions)[166] with longer alkyl side-chains, and particularly high antimicrobial activities for ILs carrying 10, 11, 12 and 14 carbon atoms in an alkoxy group. The same group[232] later reported that the antimicrobial activities of 1-alkylimidazolium and 1-alkoxymethylimidazolium lactates against rods,

cocci, and fungi strongly depend on the length of substituent (longer chain = higher activity) and the type of anion (higher activity for L-lactate than that of DL-lactate); however, the influence of ether-functionalization of substituent is not significant. Symmetrical 1,3-dialkoxymethylimidazolium ILs were reported by the same group having antimicrobial and antielectrostatic properties, and can be decomposed by aqueous solutions of $KMnO_4$.[233] The Lee group[234] confirmed that 1-alkyl-3-methylimidazolium chlorides/bromides and 1-alkyl-2-methyl-3-hydroxyethylimidazolium chlorides exhibited high antimicrobial activities against various Gram-negative bacteria, Gram-positive bacteria, and fungi, whilst *N*-alkyl-*N*-hydroxyethylpyrrolidinonium were inhibitory only to some microorganisms. The Pernak group[235] also demonstrated that choline-like salts such as quaternary ammonium chlorides derivatives of deanol esters had strong antibacterial activities over a wide range of microbial strains, which was close to the activity of benzalkonium chloride.

A series chiral ILs (Scheme 20) constituting of 3-alkoxymethyl-1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazolium cations and various anions (Cl⁻, BF_4^-, ClO_4^-, PF_6^- and Tf_2N^-) were derived from the natural chiral pool of (1R,2S,5R)-(−)-menthol, and their physicochemical properties were measured.[73] Some of these new ILs have shown high antielectrostatic and antimicrobial activities.

Hossain et al.[236] prepared eight hydroxylammonium-based protic ILs carrying carboxylate anions (formate, acetate and lactate), and found that these ILs showed different degrees of antimicrobial activities. In particular, 2-hydroxyethylammonium lactate and 2-hydroxy-*N*-(2-hydroxyethyl)-*N*-methylethanaminium acetate exhibited high antimicrobial activities against a wide range of human pathogens (such as *Staphylococcus aureus*). Choi et al.[237] synthesized dual-functional ILs including tributyl(2-hydroxyethyl)phosphonium docusate (Scheme 21) as plasticizers and antimicrobial agents for poly(vinyl chloride) in medical devices. These ILs exhibited excellent antimicrobial activity against Gram-positive bacteria, but no activity in inhibiting Gram-negative bacteria. An enhanced plasticizing effect was observed for this more polar hydroxyl-grafted IL *vs* a non-functionalized IL.

4.7 Organic reactions

The tunable solvent properties of ether- and hydroxyl-functionalized ILs have enabled their unique performance in a number of organic reactions. The primary role of these specialized ILs in organic reactions generally falls into one of three categories: reaction solvent, catalyst, and support for the catalyst or reactant.

A number of studies have demonstrated the superb solvent capability of these functionalized ILs. Dzyuba and Bartsch[135] observed that greater polarity of ether- and alcohol-functionalized ILs as solvents led to higher *endo/exo* product ratios (*i.e.*, 5.7–6.1 *vs* 4.3 for non-functionalized ILs) in the Diels–Alder reaction of cyclopentadiene with methyl acrylate. Aiming to utilize the advantages of low-melting point and low-viscosity, the Shreeve group[51, 72] synthesized oxazolidinium, morpholinium, imidazolium, and triazolium ILs grafted with alkoxy chains, and applied them as reaction media in nucleophilic trifluoromethylation reactions of trifluoromethyl(trimethyl)silane with: (i) aryl, allyl, benzyl, and alkyl halides in Cu(I)-catalyzed C–C bond formation reactions, and (ii) carbonyl functionalities, catalyzed by Ph_3P or CsF.

Sasaki et al.[238] performed glycosidations of glucopyranosyl fluoride and alcohols, using different ILs containing a Brønsted acid as the catalyst (Scheme 22). In addition to achieving high yields, high β-stereoselectivities were also obtained in both [HMIM][OTf] and [CN(CH$_2$)$_3$-MIM][Tf$_2$N]. Unfortunately, no selectivity (α/β = 52/48) was observed in an ether-substituted IL, [EtOCH$_2$CH$_2$-MIM][Tf$_2$N].

Wang et al.[239] attached a long PEG-4000 chain to an imidazolium ring through an ester linkage to form the IL [PEG-MIM]Cl which showed a melting point near 47 °C. This PEG-containing IL was found to be a suitable solvent for the $Pd(OAc)_2$-catalyzed Heck reaction of aryl bromides and activated aryl chlorides in the absence of ligands (Scheme 23), with yields generally higher than 90%. It was reported that $Pd(OAc)_2$ was readily dispersed to Pd nanoparticles in PEG under the Heck reaction conditions.[240] However, this system was less efficient for the coupling of non-activated chloroarenes. Petrović et al.[241] developed an efficient Pd(II)-catalyzed Heck reaction using triethanolammonium acetate as a reaction medium, base, precatalyst-precursor, and mobile support for the active Pd species. Density functional theory (DFT) calculations suggested that formation of two Pd(II) complexes, one of them being a 'precatalyst' producing the active Pd(0) complex.

Ding et al.[242] prepared six chiral ILs, including hydroxyl-functionalized versions, and used them as solvents for the enantioselective photoisomerization of dibenzobicyclo[2.2.2]octatrienes, achieving 3–12% *ee*. This study suggests that an ion pairing interaction of the deprotonated diacids with chiral IL cations may be responsible for the chiral induction. Prasad et al.[243] reported that benzoyl cyanide in 1-methoxyethyl-3-methylimidazolium methanesulfonate provided 'greener' and milder conditions for the benzoylation of nucleosides (both the ribo- and deoxyribo-types) at room temperature compared with conventional pyridine–benzoyl chloride system. The new benzoyl cyanide-IL system afforded the efficient benzoylation of phenols, aromatic amines, benzyl alcohol, aliphatic diols, 3-aminophenol, and 2-aminobenzylalcohol. Additionally, the new system favored the selective formation of *O*-benzoyl over *N*-benzoyl derivatives for NH_2-bearing nucleosides, which was explained by the hydroxyl group being polarized by the ether-functionalized ionic medium, becoming more nucleophilic than the amino group as a result.

A study by Wong et al.[244] suggested that the mixture of a polyoxygenated IL, ECOENG 500 (also known as Ammoeng 100, Scheme 39 in section 4.8), and an organic solvent (such as ethyl acetate) provided a suitable solvent system for Suzuki cross-coupling of phenylboronic acid and 4-bromoacetophenone catalyzed by tris(dibenzylideneacetone)dipalladium chloroform complex (Scheme 24). The advantages of this solvent mixture include: (a) high product yield (~80%), (b) high stability of the palladium catalyst in the presence of IL, (c) low solvent viscosity (78 mPa s for the 1:1 (v/v) IL/ethyl acetate mixture at 20 °C *vs.* 3150 mPa s for the neat IL). Another study on palladium-catalyzed Suzuki C–C coupling reactions was explored by using a number of ether-grafted imidazolium and pyridinium ILs (Scheme 25) as solvents.[245] Higher catalytic efficiencies were observed in these functionalized ILs than in non-functionalized ILs, which was explained by weaker interactions between the palladium catalyst and the ether groups, achieving better catalyst stabilization. Interestingly, the coupling reaction was found being influenced by the position and number of oxygen atoms in the ether side chain for imidazolium ILs, but not for pyridinium ILs.

An imidazolium IL containing a PEG-350 methyl ether chain ([MeO-PEG350-BIM][PF_6]) was prepared and used as the solvent in the $Rh(PPh_3)_3Cl$-catalyzed hydrosilylation reaction of different alkenes with triethoxysilane (see Scheme 26).[63] Quantitative conversions and high selectivities toward the β-product were achieved in the ether-functionalized IL, while less desirable performance was observed in [BMIM][PF_6] (78% conversion and 81% selectivity) and organic solvents (53–67% conversion with 66–71% selectivity). The improved reaction outcome in the new IL was attributed to the high solubility of the catalyst [*i.e.*, $Rh(PPh_3)_3Cl$] in the polyether-functionalized IL.

Alkylammonium ILs bearing two PEG-350 methyl ether tails were prepared and employed as solvents in the microwave-assisted coupling of amino acids to synthesize a variety of

dipeptides; despite the very high IL viscosity (2,230 mPa s at 25 °C), moderate to high product yields (64–95%) and excellent purities were reported, a result attributed to the hydrophilic nature of polyether-type ILs being capable of dissolving amino acids and coupling reagents.[59]

Vecchi et al.[246] studied the CuI-catalyzed cycloaddition of different combinations of azides and terminal alkynes (Scheme 27) in polyoxygenated Ammoeng 100 under amine-free conditions; this IL also enabled the synthesis of solely 1,4-disubstituted triazole regioisomers. Another study[247] revealed that in the absence of a base (such as *N,N*-diisopropylethylamine), Ammoeng 110 also yielded a high selectivity toward the 1,4-regioisomer (1,4-isomer/1,5-isomer ≈25), whilst reactions in other non-ether-functionalized ILs produced both regioisomers (although the 1,4-regioisomer was obtained in the presence of base in these ILs[247, 248]).

Zhi et al.[71] prepared an acidic PEG-1000-grafted dicationic IL (see Scheme 5) and used the mixture of this IL with toluene as a solvent system for the synthesis of 5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans *via* one-pot condensation of malononitrile, 5,5-dimethyl-1,3-cyclohexanedione, and aromatic aldehydes (see Scheme 28). This IL acted as both co-solvent and catalyst, producing higher isolated yields (82–93%) than that catalyzed by sulfuric acid (only 46% yield).

Petiot et al.[59] prepared two viscous ether-functionalized ILs, each containing two PEG-350 chains (Scheme 29). These new ILs were studied as solvents for the chemical coupling preparation of various dipeptides under microwave irradiation at 65 °C; in addition to achieving moderate to high yields (64–95%), this method enabled a short reaction time and high product purity. The polar nature of the ILs was key to the dissolution of the polar reactants (*i.e.*, amino acids) and coupling agents.

A second major advantage of ether/hydroxyl-functionalized ILs in organic synthesis entails their ***catalytic role***. For example, (3-hydroxypropyl)ammonium acetate was prepared and employed as a reusable catalyst for the condensation reaction of 4-hydroxycoumarin, aldehydes, and malononitrile to synthesize 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives at room temperature (Scheme 30); the catalyst could be reused four times without considerable loss of activity.[249]

Song et al.[250] synthesized a series of crown ether complex cation ILs (see examples in Scheme 31), and applied them as catalysts in several known reactions such as the [15-C-5Na][OH], [15-C-5Na][OAc], [18-C-6K][OH], and [18-C-6K][OAc]-catalyzed Michael addition of alkenes and relevant nucleophiles; [18-C-K][OH] and [15-C-5Na][OH]-catalyzed Henry reaction of nitromethane and aromatic aldehydes; [18-C-6K][OH]-catalyzed Knoevenagel condensation of aromatic aldehydes and malononitrile; PdCl$_2$/[18-C-6K]$_3$[PO$_4$]/K$_2$CO$_3$-catalyzed Heck reaction of olefins and aromatic halides; and [18-C-6K][BrO$_3$] acting as both oxidant and solvent in the oxidation reaction of aromatic alcohols.

Xu et al.[251] found that 1-(2-hydroxyethyl)-3-methyl imidazolium chloride was capable of catalyzing Knoevenagel condensation (Scheme 32) for a number of aromatic aldehydes with active methylene compounds under solvent-free conditions, achieving 82–97% yields. Yue et al.[252] used 2-hydroxyethylammonium acetate as a catalyst for Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate or malononitrile, achieving only *E*-isomers with yields of 83–98%. A similar study by Ying et al.[253] employed 2-hydroxyethylammonium formate as the solvent for a series of Knoevenagel condensations of aromatic aldehydes and methylene active compounds (*e.g.*, malononitrile, ethylcyanoacetate,

cyanoacetamide). The reactions were conducted at room temperature, required no additional catalyst, and generally produced yields in excess of 90% within 2–8 h.

Two different groups synthesized cyclic carbonates by a cycloaddition reaction of epoxides with CO_2 (Scheme 33a) catalyzed by either free hydroxyl-containing ILs,[256] or hydroxyl-containing ILs supported on polystyrene (PS)[254] or poly(divinylbenzene) (PDVB)[255] polymeric beads (see Scheme 33b,c). The first group[254, 256] reported high yields (80–99%) and high selectivities (92–99%) of cyclic carbonate formation under mild conditions (2.0–2.5 MPa, 120–125 °C, and 1.6 mol% catalyst) without any co-solvent, and the catalyst could be reused six times without appreciable loss of activity. The second group[255] achieved nearly quantitative yields of carbonates (2.0 MPa of initial CO_2, 140 °C, and 0.44 mol% catalyst) coupled with high selectivities (>99%) under solvent-free condition. A synergetic effect between the bromide ions and the hydroxyl groups in promoting the coupling reaction was also noted.

The third role of ether- and alcohol-functionalized ILs involves their promise as ***novel fluidic supports for catalyst or reactant***. Hakkou et al.[257] used a supported hydroxylated ILs methodology, so-called IL phase organic synthesis (IoLiPOS), for the multi-step preparation of 2-thioxo tetrahydropyrimidin-4-(1*H*)-ones (Scheme 34): (i) esterification of hydroxyl-containing ILs **1** with acryloyl chloride **2** to form IL-bound acrylate **3** in quantitative yield; (ii) Michael addition of aliphatic primary amines **5** to **3** to afford β-aminoesters **6** in high yield; (iii) addition of alkyl isothiocyanates **7** to **6**, yielding thioureido esters **8**; and (iv) cyclization-cleavage under basic conditions to produce 2-thioxo tetrahydropyrimidin-4(1*H*)-ones **9**. This method is advantageous since the byproduct can be easily removed by extraction and washing from the cleaved IL phase and standard analytical methods (*e.g.*, NMR, TLC) can be used to monitor the reaction progress, in contrast to the analysis restrictions imposed by solid-phase synthesis. The 'IL phase organic synthesis' technique was also used by the same group[258] to prepare a number of 4-thiazolidinones under microwave irradiation.

Hydroxyl-functionalized ILs were used as supports for the catalyst quinuclidine (*via* a covalent linkage to the amine group in ILs) in Baylis–Hillman reactions (Scheme 35).[259] The new catalysts demonstrated higher catalytic activities compared with catalysts immobilized on non-functional ILs, and the new catalysts were easily recycled and reused at least six times without significant loss in catalytic activity. Another recent study[54] prepared trialkyl(2,3-dihydroxypropyl)phosphonium ILs, and utilized them as additives (catalysts) in the Baylis–Hillman reaction, doubling the product yields by adding 10 mol% of the hydrophobic trioctyl(2,3-dihydroxypropyl)phosphonium hexafluorophosphate.

In contrast to solid-phase synthetic strategies, Miao and Chan[260] utilized a hydroxyl-grafted IL as a novel soluble support for the synthesis of oligopeptides (Leu[5]-enkephalin) (Scheme 36). This approach has several advantages, including the reduced use of reaction reagents, facile purification of intermediates through solvent washing, high loading capacity, and low support cost when compared to fluorous or polymer supports.

Sometimes, functionalized ILs may serve multiple roles in a reaction. For instance, Richter et al.[261] used *N*-(2-hydroxyethyl)ammonium formate as a solvent, as well as a reducing and templating agent for the microwave-assisted preparation of a macroporous silver framework from $AgNO_3$; this approach produced pure products and required a mild reaction temperature of only 80 °C.

4.8 Protein/Enzyme Stabilization and Activation

As alluded to previously, the molecular structures of the cation and anion paired to form an IL considerably influence the solvent features and, careful balance is crucial to achieve stabilizing enzyme/IL interactions. These properties certainly include, but are not limited to, the polarity, hydrogen-bond basicity, anion nucleophilicity, the liquid-phase nanostructure of the IL, kosmotropicity, viscosity, and hydrophobicity. Therefore, it is important to customize the structures of ILs for particular biocatalytic applications based upon the available knowledge correlating IL structure with enzyme activity. Indeed, a number of studies have sought to tailor the IL ion structures to dictate the favorable compatibility with enzymes.

Park and Kazlauskas[216] discovered that the solubility of D-glucose in $[(CH_3OCH_2CH_2)-MIM][BF_4]$ was about 5 mg/mL, about 100 times higher than that in acetone or THF. The CALB-catalyzed acylation of D-glucose with vinyl acetate in this ether-functionalized IL was fast and highly selective (99% conversion and 93% monoacylation) compared with reactions in other non-functionalized imidazolium and pyridinium ILs. Kim et al.[262] demonstrated that the enzymatic acylation of monoprotected glycosides with vinyl acetate catalyzed by *Candida rugosa* lipase was faster and more selective in ILs ($[BMIM][PF_6]$ and $[CH_3OCH_2CH_2-MIM][PF_6]$), which was attributed to the high substrate solubilities in ILs and more favorable enzyme adaptation in polar ILs. Lozano et al.[263] reported a lower CALB activity and stability but a higher selectivity in $[(HOCH_2CH_2CH_2)-Me_3N][Tf_2N]$ compared to non-functionalized ammonium ILs during the enantioselective transesterification of 1-phenylethanol and vinyl propionate. Itoh et al.[264, 265] prepared new imidazolium ILs carrying functionalized anions of polyoxyethylene(10) cetyl sulfate (Scheme 37), and used them as either additives or lipase-coating-agents in the *Pseudomonas cepacia* lipase-catalyzed transesterification of a variety of secondary alcohols (such as 1-phenylethanol) with vinyl acetate carried out in diisopropyl ether or hexane; both preparations greatly improved the reaction enantioselectivity while the lipase-coating approach also increased the reaction rate. MALDI-TOF mass spectrometry further confirmed the binding between functionalized IL and the protein in IL-coated lipase PS.[265]

Walker and Bruce[266] developed a hydrophilic IL, namely 1-(3-hydroxypropyl)-3-methylimidazolium glycolate (Scheme 38), as the solvent for homogeneous chemical catalysis and biocatalysis. The hydroxyl-functionalized IL was found capable of dissolving both morphine dehydrogenase and its cofactor nicotinamide, and maintaining high enzymatic activity in converting codeine to codeinone. The same IL was further used to establish the codeinone/neopinone equilibriation and the hydration of the neopinone double bond to form oxycodone *via* bis(acetylacetonato)cobalt (II) catalysis. Turner et al.[267] studied the stability of human serum albumin (HSA) in aqueous solutions of ILs by fluorescence and CD spectroscopy, and found the hydroxyl/ether-functionalized imidazolium ILs to be less protein-denaturing than [BMIM]Cl, which was explained due to the likely favorable H-bond interactions between ILs and the protein.

The Xu group[268–273] selected a group of commercial tetraammonium-based ILs as reaction media for enzymatic glycerolysis. As shown in Scheme 39, each of these ILs is an ionic mixture containing multiple alkyloxy groups, which have both hydrophilic and hydrophobic character. In particular, Ammoeng 100 (also known as $[CPMA][MeSO_4]^\ddagger$) and 102 are capable of dissolving triglycerides and were shown to be lipase compatible during glycerolysis reaction;[269, 270] trioctylmethylammonium bis(trifluoromethylsulfonyl)imide ($[TOMA][Tf_2N]$) and its mixture with Ammoeng 102 have also been demonstrated as

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‡From the name of cocosalkyl pentaethoxy methylammonium methylsulfate.

suitable solvents for enzymatic glycerolysis.[272–274] De Diego et al.[275] have further demonstrated the higher transesterification activities of both free and immobilized CALB in [CPMA][MeSO$_4$] than in several PF$_6^-$ and BF$_4^-$ based ILs; however, two other lipases from *Thermomyces lanuginosus* (TLL) and *Rhizomuncor miehei* (RML) appeared less active in [CPMA][MeSO$_4$] than in PF$_6^-$ or BF$_4^-$ based ILs. Xu and co-workers[269, 271] utilized the conductor-like screening model for real solvents (COSMS-RS) to derive various parameters (such as misfit, H-bonding and van der Waals interaction energy) to understand the multiple interactions in ILs; the model also provides guidance in designing the structures of cations and anions.[276] The Bolm group[277] deployed oxygen-containing ILs (such as the Ammoeng series and [C$_2$OHmim]Cl) as additives in the enantioselective hydrolysis of diester malonates catalyzed by pig liver esterase (PLE), and observed that less than 1% ILs in combination with 10% isopropanol/water were sufficient to improve both the activity of PLE (up to 4-fold) and the enantioselectivity.

The Goto group covalently immobilized *Candida rugosa* lipase[278] and subtilisin Carlsberg[279, 280] onto an unusual comb-shaped PEG (so-called PM$_{13}$). Both solubilized PM$_{13}$-lipase[278] and PM$_{13}$-subtilisin[280] were found highly active and stable in Tf$_2$N$^-$ based ILs, although these enzymes were more active in the more hydrophobic IL [EMIM][Tf$_2$N] than in functionalized ILs like [(CH$_3$OCH$_2$CH$_2$)-MIM][Tf$_2$N] and [(HOCH$_2$CH$_2$)-MIM] [Tf$_2$N]. Based on the lyoprotectant effect of tris(hydroxymethyl)aminomethane (Tris) as an excipient in horseradish peroxidase lyophilization,[281] Das et al.[282] mimicked the structure of Tris and rationally designed the new IL tetrakis(2-hydroxyethyl)ammonium triflouromethanesulfonate (Scheme 40). These authors found that horseradish peroxidase in this new IL was an order of magnitude more active than in methanol and some 30–240-fold more active than in conventional ILs. The Itoh group[283] synthesized an alkyloxy-containing hydrophobic IL named 2-methoxyethyl(tri-*n*-butyl)phosphonium bis(trifluoromethane)sulfonamide ([MEBu$_3$P][Tf$_2$N]), and observed a faster reaction rate for lipase PS-catalyzed transesterification of secondary alcohols in this IL than in diisopropyl ether. This group[284] further rationally designed 2-methoxyethoxymethyl(tri-*n*-butyl)-phosphonium bis(trifluoromethanesulfonyl)amide ([P$_{444MEM}$][Tf$_2$N]) as an 'enzyme-benign' solvent for IL-coated lipase PS-catalyzed acylation of secondary alcohols with vinyl acetate, obtaining high enzymatic activities and selectivities. Lourenço et al.[285] noted little Novozym® 435 activity in the denaturing IL [BMIM][dca], wheras reasonable activity and enantioselectivity were seen in [aliq][dca] [aliq = trioctylmethylammonium (Aliquat 336®)]. One plausible explanation is that the denaturing anion's molar concentration in [aliq][dca] is much lower than that in [BMIM][dca] due to much higher molar mass of aliq$^+$ relative to BMIM$^+$.[67, 218, 286] Vafiadi et al.[287] employed two functionalized ILs [C$_2$OHmim][PF$_6$] and [C$_5$O$_2$mim][PF$_6$] as solvents for the feruloyl esterase-catalyzed esterification of glycerol with sinapic acid, and achieved comparably high yields (72.5% and 76.7%, respectively) in these two different ILs under optimal conditions. These relatively low-viscosity ILs can be considered as amphiphilic solvents, in that they contain a hydrophilic cation paired to a hydrophobic anion.

Recently, the Zhao group[67] rationally synthesized a series of alkyloxyalkyl-containing ILs based on acetate (Scheme 18). It was found that these ILs could be designed to dissolve many substrates (including cellulose, sugars, glucose, ascorbic acid, amino acids, betulinic acid, fatty acid, and triglycerides) that are not readily soluble in common organic solvents.[67, 218, 219, 225, 288] In addition, these ILs can be optimized to be compatible with CALB, and thus become ideal solvents for producing the derivatives of many substrates via enzymatic reactions.[67, 218, 288] Therefore, it is clearly possible to manipulate the structures of ILs to make them more compatible with enzymes, and to be able to dissolve a variety of compounds. This could significantly improve the biocatalytic efficiency of many reactions as several important substrates are not soluble in conventional organic or aqueous media.

The Petrich group[289] identified that *Tricoderma reesei* cellulase was stable in tris-(2-hydroxyethyl)methylammonium methylsulfate even at temperatures near 100 °C, but denatured in pH 4.8 citrate buffer at about 50 °C based on fluorescence spectroscopy and DSC measurements. Unlike imidazolium ILs, this ammonium IL does not appear to quench tryptophan fluorescence. However, as pointed out by that study,[289] the fluorescence quenching of aromatic amino acids in enzymes is not always associated with enzyme denaturation, a notion in agreement with observations by other groups as well.[218, 290]

Six monoether-functionalized imidazolium ILs carrying anions of Tf_2N^- or PF_6^- were prepared and employed in the lipase-catalyzed kinetic resolution of secondary alcohols.[291] Higher enantioselectivities (95–99% *ee*) were observed in some ether-functionalized ILs than those in diisopropyl ether or non-functionalized ILs ([BMIM][BF_4] and [BMIM][PF_6]). Different structures of these customized ILs play an important role in the resolution reaction, which can be related to how the ether groups interact with the enzyme and substrates, and how the ether groups tune the hydrophilic nature of the solvent environment. Ståhlberg et al.[292] found that glucose isomerase was active in catalyzing the isomerization of glucose to fructose in *N,N*-dibutylethanolammonium octanoate containing 20 wt% water; however, the enzyme was inactive in other alkanoate-based ILs, including formates, acetates, and propionates.

To improve the activity of formate dehydrogenase (FDH) from *Candida boidinii* in [MMIM][Me_2PO_4], Bekhouche et al.[293] covalently linked hydroxyl groups in three ILs to the enzyme lysine residues via carbamate linkages. These three ILs included cholinium dimethyl phosphate, 1-(2-hydroxyethyl)-3-methylimidazolium chloride, and 1-(2-hydroxypropyl)-3-methyl imidazolium chloride (Scheme 41). The chemically-modified FDH still retained 30–45% of its activity in 70 vol% [MMIM][Me_2PO_4] whilst the native enzyme was inactive in this solution. This particular enzyme modification also improved FDH's stability, in terms of the 'half-time' ($t_{1/2}$) in aqueous solution, by three to five times, although both modified and unmodified enzymes exhibited increased $t_{1/2}$ values in 37.5 vol% [MMIM][Me_2PO_4].

Different ILs were used as additives in the sol–gel immobilization of α-rhamnosidase and β-glucosidase expressed by naringinase, and a higher α-rhamnosidase efficiency was observed in more hydrophobic ILs (*i.e.*, the order of activity was [BMIM][BF_4] > [(HOCH_2CH_2)-MIM][BF_4] > [BIM][BF_4]); the addition of [OMIM][Tf_2N] and [(HOCH_2CH_2)-MIM][PF_6] was found to reduce enzyme deactivation in tetramethylorthosilicate (TMOS)/glycerol matrices.[294] No CALB activity was observed in the denaturing IL [BMIM][NO_3] during the transesterification of ethyl butyrate and 1-butanol, but some activities was noted for hydroxyl-functionalized ILs (*i.e.*, [(HOCH_2CH_2)-MIM][NO_3] and [(HOCH_2CH_2)-MIM][BF_4]), with a higher activity seen for the latter) and such activities were further improved two to five fold by the addition of a so-called 'IL buffer' [BMIM][H_2PO_4].[295] The fluorescence spectra suggest that hydroxyl group-containing ILs are capable of maintaining the native compact structure of the enzyme.

Using near-UV CD measurements, Mann et al.[296] examined the thermal stability and refolding ability of lysozyme in aqueous ILs, and found some interesting patterns: both ethylammonium formate and 2-methoxyethylammonium formate were effective refolding agents, whilst propylammonium formate becomes an effective refolding additive at concentrations up to ~62.5 wt% but causes protein denaturation at higher concentrations. Meanwhile, ethanolammonium formate was shown to be capable of stabilizing lysozyme against unfolding at high temperature, and a nearly complete renaturation upon cooling was observed. Up to 6-fold higher lysozyme activities were seen in aqueous solutions of ethanolammonium formate. This was rationalized by the hydroxyl-functionality of the IL presenting additional H-bonding donor/acceptor sites to reduce undesired hydrophobic

interactions between the IL and the protein. However, no improvement in protein thermal stability was detected in 2-methoxyethylammonium formate solutions, since the ether oxygen only acts as a hydrogen bond acceptor and an extra hydrogen bond donor group appears to be a key factor in protein stabilization. The Bruce group[290] noticed that subtilisin remained active when being dissolved in diethanolammonium chloride, but was inactive in other protic hydroxylalkylammonium ILs. Complicating matters, chymotrypsin was not active in either IL. Although fluorescence spectroscopy failed to show the differences, far- and near-UV signals for subtilisin in diethanolammonium chloride matched well with the signature in water, suggesting the integrity of secondary and tertiary structures when dissolver in this hydroxyl-grafted IL.

Using molecular dynamics (MD) simulations, Klähn et al.[297] suggested that the polar methoxyethyl group and a decyl aliphatic chain on the IL cation are stronger CALB destabilizers than non-functionalized and shorter (methyl) groups, respectively. However, they apparently destabilize the protein *via* two distinct mechanisms: the methoxyethyl group interacts with CALB by strong Coulombic interactions to destabilize the protein surface, whereas the long alkyl chain induces a direct interaction between IL molecules and the protein's hydrophobic core.

In addition to their major uses as reaction media, some functionalized ILs can be incorporated into the substrate to facilitate an enzymatic reaction. For example, Naik et al.[298] attached ibuprofen to a hydroxyl group in a PF_6^- based IL, and subsequently hydrolyzed the anchored ibuprofen by lipases in a 50/50 (v/v) mixture of organic solvent (or [BMIM][PF_6]) and 0.1 M phosphate buffer (Scheme 42). When the reaction in DMSO/buffer was catalyzed by CALB, (*S*)-ibuprofen was obtained with 86% *ee* and 87% isolated yield. The same CALB-catalyzed reaction carried out in [BMIM][PF_6]/buffer gave 80% *ee* with 80% isolated yield. The anchored substrate also simplifies post-reaction separation since the substrate is soluble in the reaction media and the hydrolyzed enantiomer can be easily extracted by diethyl ether.

In summary, it is emerging that enzyme-compatible ILs appear to share some common structural features: (1) they are frequently characterized by relatively large molecular structures to effectively minimize H-bond basicity and anion nucleophilicity effects; (2) they often contain multiple ether and/or alcohol functionality so that the solvent properties (*e.g.*, viscosity, H-bond basicity, affinity for water) are optimized, giving rise to mild IL/enzyme interactions. In addition, the high enzyme activity in ether-functionalized ILs is also due, in part, to the special features of the ether chain itself. A very recent study[102] suggests that cations of imidazolium and pyridinium form stable complexes with PEG-800 or PEG-1000 via ion–dipole interactions; in effect, the cations are 'wrapped' by PEG molecules. It is also known that alkoxy chains in ether-functionalized ILs are more flexible than rigid alkyl chains,[99] and the incorporation of an ether chain reduces the intermolecular correlation (particularly tail–tail segregation) and cation–anion specific interactions.[101] Therefore, in ether-functionalized ILs, the cations are expected to interact (intramolecularly and/or intermolecularly) with the ether chain, which preferentially reduces cation–protein interactions. As a result, the ether-functionalized ILs are more enzyme compatible than alkyl substituted ILs. On the other hand, the role of anions in ether-functionalized ILs becomes very important for enzyme stabilization: if the anions are enzyme-denaturing (notorious examples include the halides, dca⁻, and acetate), their molar concentration must be reduced,[67, 218] unless they are used as kosmotropic salts in dilute solutions.[299] Otherwise, the anions must be neutral (such as for Tf_2N^- or PF_6^-) in terms of H-bond basicity, and should not be highly acidic, basic, or nucleophilic.[11]

4.9 Nanomaterials applications

Recently, innovations in IL science have been coupled with nanotechnology to produce nanomaterials with improved catalytic, optical, electrical, magnetic, biological, or biomedical properties. Several general reviews on nanomaterials synthesis using ILs are available in the literature.[300, 301] Here, we will briefly highlight the role that ether- and hydroxyl-functionalized ILs have to play within nanoscience.

4.9.1 Stabilizers or dispersants for nanoparticles—Functionalized ILs (sometimes along with ionic polymer additives) can stabilize the dispersion of nanoparticles (NPs) to improve their performance. For example, 1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate, was used as a solvent and a stabilizing agent in the preparation of gold(0) nanoparticles (GNPs) via hydrazine reduction of a chloroauric acid solution.[302] The imidazolium cation is thought to be the major stabilization factor for the GNPs in this example, but the 1-triethylene glycol monomethyl ether tail prevents further aggregation by pointing away from the GNP surface to act as a steric barrier between GNPs and GNP aggregates. Thus, an electrosteric stabilization mode was proposed as summarized in Fig 1.

Yang et al.[303] observed that hydroxyl-functionalized ILs could dissolve and stabilize polyvinyl pyrrolidone (PVP)-stabilized rhodium (Rh) nanoparticles, which enables an effective and highly stable catalytic system for biphasic hydrogenation reactions. Such stabilization was not witnessed in non-functionalized ILs such as $[C_2mim][BF_4]$, while hydroxyl-functionalized ILs efficiently dispersed the PVP-protected Rh nanoparticles (Fig 2). As a result, the catalytic activity in all hydroxyl-containing ILs for styrene hydrogenation was considerably higher (80–99% yields) than that observed in $[C_2mim][BF_4]$ (21.5% yield).

Ueno et al.[304] dispersed hydrophilic and hydrophobic silica nanoparticles in BF_4^- based ILs and in the hydroxyl-containing IL 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethane sulfonyl)amide ($[C_2OHmim][Tf_2N]$). It was found that the rheological behavior of the colloidal dispersion was strongly dependent on the ionic structures of the ions comprising the IL. In this case, the BF_4^- anion and $[C_2OHmim]^+$ cation interacted with the silica surface through H-bonding, strengthening the steric hindrance derived from the ions themselves.

Yu et al.[305] electrodeposited Au/Pt alloy nanoparticles in the 2.5±0.2 nm size range onto a $[C_3(OH)_2mim][BF_4]$ film with no agglomeration. The presence of the hydroxyl groups on the imidazolium ring facilitated the donation of electrons to the hybrid orbitals of the metal ions, forming small, well-dispersed nanoparticles. Glutamate oxidase (GlutaOx) was further immobilized on these nanoparticles to construct a GlutaOx-$[C_3(OH)_2mim][BF_4]$-Au/Pt-Nafion biosensor, which showed a good electrocatalytic response to glutamate at a potential of −200 mV, demonstrating a promising *in vivo* application for on-line microdialysis.

4.9.2 Both reductants and stabilizers for synthesis of nanoparticles—In some cases, hydroxyl-functionalized ILs are not only excellent stabilizers of nanoparticles (due to the coordination between ILs and NPs), but they can also function as weak reducing agents for NP synthesis due to the presence of oxidizable hydroxyl groups. In a recent example, hydroxyl-functionalized ILs and hydroxyl-functionalized cationic surfactants acted both as the reductant and effective stabilizer for the synthesis of uniform monodisperse crystalline Ag nanoparticles with a one-phase method.[306] These ILs and surfactants (Scheme 43) were designed to bear one or two alcohol groups and different long-chain structures for producing small nanoparticles with different sizes. The CH_2OH group in these ILs was oxidized to CHO by reducing Ag^+ ion to Ag^0 during the formation of Ag NPs. Strong coordination with

the alcohol's oxygen atom(s) and with the C-2 proton of the imidazolium ring are thought to be essential to achieving uniform 2–8 nm sized Ag NPs. Transmission electron microscopy (TEM) images show that Ag nanoparticles are well dispersed in the ILs and the NP size becomes smaller with an increase of number of hydroxyl groups in ILs.

Similarly, the solvothermal synthesis of Ni NPs from nickel acetylacetonate was carried out in a hydroxyl-functionalized IL, 1-methyl-3-(2-hydroxylethyl)imidazolium tetrafluoroborate ([C_2OHmim][BF_4]), which served double duty as reducing agent and stabilizer.[307] The nanoparticle size was finely tunable by properly adjusting the IL concentration as well as the reaction time and temperature. In addition, the Ni particles prepared in the IL at 180 °C for 6 h exhibited a strong electrocatalytic capability over the oxidation of calcium 2,5-dihydroxybenzenesulfonate (CDBS). Bouvy et al.[308] showed that whereas micron-sized Au sheets were primarily prepared in non-functionalized ILs following an ionothermal approach, the use of an alcoholic IL ([C_2OHmim][Tf_2N]) yielded only Au microspheres.

A new type of ionic photosensitizer, cholinium-purpurin-18 (Chol-Pu-18), was synthesized by the Shim group.[309] Small Au NPs of average size 8–25 nm were prepared and stabilized in this photosensitizer.[309] In this case, gold ions were reduced by the hydroxyl group in choliniumpurpurin-18. The ionic photosensitizer-stabilized nanoparticles have potential applications in photodynamic therapy (PDT) or photothermal therapy (PTT) of cancer as well as in the screening of cancerous cells.

In summary, functionalized-ILs may have desirable effects for the controlled creation of nanomaterials, such as limiting the diffusion of nanoparticles, tuning the structure of nanoparticles, and improving physicochemical characteristics of the resulting nanoparticles. Additionally, hydroxyl-functionalized ILs can also act as reducing agents during the preparation of nanomaterials. We anticipate that functional ILs will be an important addition to the nanochemist's toolkit, and future rapid advances can be expected in this area.

4.10 Other applications

A series of dicationic ILs functionalized with PEG chains paired with the Tf_2N^- anion were recently evaluated as potential high-temperature lubricants because of their high thermal stability (T_d > 415 °C for imidazolium type) and excellent tribological characteristics even at 300 °C.[60] Recently, silica xerogels were prepared with various morphologies via the sol–gel method in the presence of ether-functionalized ILs (such as 1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate); these ILs act as both morphology controller and acid pre-catalyst.[310, 311]

Lu et al.[312] prepared and tested gas chromatography (GC) capillary columns coated with either functionalized ILs ([$HO(CH_2)_6$-BMIM][Tf_2N] or [$HO(CH_2)_8$-BMIM][Tf_2N]) or a conventional, non-functionalized IL ([BOIM][Tf_2N]) as potential stationary phases. Examination of the resulting separations for a variety of organic compounds (*e.g.*, alkanes, esters, alcohols, dimethoxybenzene) revealed that hydroxyl-appended ILs produced much better baseline separation, higher peak symmetry, greater selectivity, and improved thermal stability compared with columns produced from an ordinary IL. It was suspected that the hydrogen-bonding capability of hydroxyl groups played an essential role in these improvements. Breitbach and Armstrong[82] investigated a number of high thermal stability phosphonium ILs, including an ether-functionalized dicationic IL as stationary phase for gas–liquid chromatography (GLC), and indicated that different solvent properties of phosphonium ILs from alkylammonium ILs enable favorable separation selectivities. Twu et al.[148] studied various ether/hydroxyl-functionalized and nonfunctionalized ILs as GC stationary phases, and reported that the retention behaviors of probe molecules in these IL-coated stationary phases serves as an excellent tool for examining the solvation

characteristics and polarity of the ILs (see section *3.5. Polarity, hydrophilicity, and H-bonding capability*).

Blanco et al.[313] studied the lubrication effect to TiN plasma vapor deposition (PVD) coating by ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate as 1 wt% additive in a polyalphaolefin (PAO 6). Tribological tests suggested that the functionalized IL improved the anti-friction and anti-wear behaviors of the base oil, but its performance is poorer than the traditional zinc dialkyldithiophosphate (ZDDP). The tribological improvement was attributed to the tribofilms formed from the interaction of the IL with the surface, as confirmed by interferometry and XPS measurements.

In a highly innovative application, Kawai et al.[314] prepared several choline-like hydrophilic ILs (hydroxyl- and/or carboxyl-functionalized ammonium ILs with CH_3SO_3- as the anion), and showed their potential for visualizing samples by scanning electron microscopy (SEM), including hydrated samples such as seaweed and foodstuffs. It was found that this sample treatment prior to SEM analysis allows for the visualization of samples without charging and without metal sputtering. It was further observed that these choline-like ILs were capable of replacing some water molecules within the sample's cells, whereas imidazolium ILs could not.

The IL crystal (ILC) mesomorphic properties of *N*-(2-hydroxypropoxy) trimethyl ammonium-based ILs were also recently studied,[315] and it was found that the inclusion of a 2-hydroxypropoxy group enabled a bent configuration for the alkyl chain relative to the ammonium headgroup, weakening the N^+–X^- ionic attractions and H-bonding within the ionic layers. It was also noticed that different anions (Br^- or BF_4^-) impose a significant impact on the phase properties of ILCs, such as phase transition temperatures, crystallization rate, layer spacing, and structural strength.

Choline-based ILs have also gained some notoriety for some highly unusual or niche applications (in addition to their antimicrobial applications which will be described in section 4.6), including the use of choline-derivatives like alkoxymethyl(2-decanoyloxyethyl)dimethylammonium bis(trifluoromethylsulfonyl) as formalin-replacing fixatives for soft tissues,[166] choline hydroxide as a base catalyst for converting propylene oxide to 1-methoxy-2-propanol,[168] use of choline proline on heat-treated mesoporous carbons for catalyzing the Michael reaction between cyclohexanone and β-nitrostyrene,[169] choline formate as both an initiator and a solvent for the polymerizations of vinyl and methacrylate monomers,[170] and [choline][Tf$_2$N] as a proton acceptor in a fast intermolecular proton transfer between the cation's hydroxyl group and an acid [1,1,1-trifluoro-*N*-(trifluoromethylsulfonyl)methanesulfoneamide].[316]

5. Anion-Functionalized ILs

As discussed above, most ether/hydroxyl-functionalized ILs are cation-modified; however, there are also examples where the functionality is incorporated into the anion structure. For example, ionic melts formed by pairing polyether-tailed 2-sulfobenzoate with ruthenium hexamine, metal trisbipyridines, or porphyrin derivatives allow microelectrode voltammetry directly in the undiluted material.[66] Activity coefficients at infinite dilution for 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy) ethyl sulfate were measured and these data were analyzed for the separation of hexane/benzene mixtures.[317] 1-Methyl-3-octyl-imidazolium diethylenglycolmonomethylether sulfate (ECOENG 48M) was studied as the solvent for the Suzuki cross-coupling of phenylboronic acid and 4-bromoacetophenone.[244] 1-Ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate was used as a solvent for the extraction of linalool from citrus essential oil.[318] Klein et al.[319] prepared quaternary ammonium salts (including choline salts) of an oligoether carboxylate (2,5,8,11-

tetraoxatridecan-13-oate) (Scheme 44) with a T_g of −60 °C and viscosities in the range of 260–840 mPa s at 25 °C; these organic liquids exhibit significantly lower viscosities, higher conductivities, and higher polarities than alkali oligoether carboxylates.

6. Other Sulfur- and Oxygen-Functionalized ILs

Thiol/thioether functionality (also see review[320])

Lee et al.[321] demonstrated the formation of self-assembled monolayers (SAMs) of thiol-grafted imidazolium ILs on a gold surface, and observed the strong influence of IL anions on the surface hydrophobicity and wettability. Furthermore, the same group[322] indicated that SAM surfaces coated with these ILs on a gold electrode exhibited a selective electron-transfer toward redox-probe molecules: that is, the electron transfer was observed in the presence of $Fe(CN)_6^{3-}$ but not in the case of $Ru(NH_3)_6^{3+}$. Similarly, Rong et al.[323] immobilized a thiol-functionalized imidazolium IL on the surface of a gold electrode via Au–S bonds, and observed more intense and stable electrochemiluminescence (ECL) for the luminol-O_2 system at the Au–IL and water interface. Itoh et al.[324] reduced a disulfide-functionalized imidazolium salt to thiol with *in situ* formation and stabilization of Au NPs (Scheme 45). The thiol-IL stabilized Au NPs were water soluble and stable against Brønsted acids such as HCl, HBr and HBF_4. However, when either HI or HPF_6 was added, agglomeration of nanoparticles along with a color change of the solution was observed, suggesting potential applications in optical sensors for anions.

A pyrrolidinium IL incorporating a thioether-functionalized chain was prepared, and its polarity (E_T^N) and three Kamlet–Taft parameters determined.[325] This study suggested that the thioether-containing IL had a lower polarity and α value (H-bond acidity), but a higher π* value (dipolarity/polarizability) than alkyl- and cyano-substituted ILs. Tindale et al.[326] reported the synthesis of thiol-terminated fluorinated phosphonium ILs and their uses as superhydrophobic coatings; the thiol groups enabled ILs to deposit on rough silver surfaces *via* covalent bonds to form durable and non-wetting ionic films. Lesniewski et al.[327] constructed a gold–carbon nanoparticulate film electrode from oppositely-charged conductive particles using a layer-by-layer approach, and observed that the use of a thiol-functionalized imidazolium salt as nanoparticle stabilizer (instead of amino groups) required no protonation during the assembling process. Two anion-functionalized ILs (*i.e.*, 1-methylimidazolium mercaptopropionate and bis(1-methylimidazolium) mercaptosuccinate) were studied as interfacial modifiers for styrene butadiene rubber/halloysite nanotubes (SBR/HNTs) composites; their affinity toward HNTs was attributed to hydrogen bonding whilst the grafting reactivity onto SBR chains was ascribed to a thiol–ene reaction.[328] The incorporation of ILs allowed vulcanization and better dispersion of HNTs within the rubber matrix, strengthening the mechanical properties of the resulting composites. The same group[329] further employed 1-methylimidazolium mercaptopropionate as a modifier for styrene–butadiene rubber/silica composites, where the IL forms H-bonds with silica and again reacts with the double bonds of rubber *via* thiol–ene chemistry. As a result, the mechanical strength and abrasion resistance of the modified vulcanizates were greatly improved due to the increased interfacial interaction.

Carboxyl functionality

Zhao et al.[149] suggested that the incorporation of an ester group onto an IL cation increases the solvent's H-bond acidity due to the weakly acidic α-protons next to the ester group. Methylcarboxyl or cyano group substituted imidazolium ILs were investigated as electrolytes in lithium batteries.[330] Imidazolium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium salts of Tf_2N^- functionalized with carboxyl groups were used in the selective dissolution of metal oxides and hydroxides.[146] Activity

coefficients at infinite dilution of various organic compounds in two ester-functionalized ILs (*n*-methacryloyloxyhexyl-*N*-methylimidazolium bromide and *n*-acryloyloxypropyl-*N*-methylimidazolium bromide) were measured by the inverse GC method.[331] The grafting of polar substituents to the cation had a strong impact on the thermodynamic behavior of organic compounds within mixtures with the IL. As a result, a high selectivity was observed in the separation of aliphatic hydrocarbons from aromatic hydrocarbons by using these ILs when compared with traditional organic solvents. Wang et al.[332] covalently attached a carboxylic acid-functionalized IL, 1-(methylcarboxylic acid)-3-octylimidazolium bis(trifluoromethylsulfonyl)imide), to an oxidized boron-doped diamond (BDD) surface via an esterification reaction; the IL-modified electrode was found capable of selective electron transfer towards positive and negative redox species: $Fe(CN)_6^{4-}$ was detected on the IL-modified BDD interface, but surface-adsorbed $Ru(NH_3)_6^{3+}$ was not detected. Tsuda et al.[333] prepared a piperidinium IL ($T_g = -24.3$ °C) functionalized with propylene carbonate (see Scheme 46) as potential electrolyte for energy-storage devices (ESD) because of its high thermal stability and lithium metal deposition ability, although this IL exhibited a high viscosity (~29,000 mPa s at 40 °C) and low conductivity (0.007 mS/cm at 40 °C). Deng et al.[104] suggest that the incorporation of an ester functionality to the alkyl chain of pyridinium or ammonium cations (Tf_2N^- as anions) increases the viscosity by 5 folds for pyridinium ILs and 2 folds for ammonium ILs at 20 °C.

An ester-functionalized can be used an ionic acylating agent in the enzymatic resolution of secondary alcohols carried out in ILs (such as [BMIM][PF$_6$] and [BMIM][BF$_4$]).[334] As illustrated in Scheme 47, during the first step, (*R*)-alcohol in the racemic mixture reacts with the ionic acylation agent while the remaining (*S*)-enantiomer is removed *via* extraction; in the second step, the ionic acylation agent was regenerated by reacting with ethanol and the released (*R*)-alcohol is obtained *via* extraction. The main advantage of this approach comparing to other methods is the simple separation of both free enantiomers by enzymatic resolution in a one-pot reaction through one equivalent of acylating agent. Moderately high *ee* (50–81%) were obtained for (*S*)-alcohol, while very high *ee* (91–99%) were achieved for (*R*)-alcohol.

Diketonate functionality

Due to the coordination property of acetylacetone derivatives (upon deprotonation) as ligands, Olivier et al.[335] designed trifluoromethyl-1,3-diketonate-functionalized ILs carrying different counter-anions (BF$_4^-$, PF$_6^-$ and Tf$_2$N$^-$) (Scheme 48), and employed them in the extraction of lanthanide salts (Eu, Tb) from dilute aqueous solutions. Their study reveals that immobilization of these ILs onto silica particles pretreated with dilute aqueous NaOH solutions produced rapid and nearly quantitative (>99.9%) extraction of metal ions (as their diketonato complexes); the method was also reported being reproducible and simple in recovering metal ions and ILs.

7. Choline-Based Deep Eutectic Solvents and Their Applications

Recently, the Abbott group[336–338] has demonstrated that a mixture of solid organic salt and a complexing agent can form a liquid at temperatures below 100 °C, so-called deep eutectic ILs (DESs). The mechanism is that the complexing agent (typically a H-bond donor) interacts with the anion and increases its effective size, which in turn reduces the anion interaction with the cation and thus decreases the freezing point (T_f) of the mixture. A typical example is the mixture of choline chloride (m.p. = 302 °C, 2-hydroxyethyl-trimethylammonium chloride, Scheme 49) and urea (m.p. = 133 °C) in a 1:2 molar ratio resulting in a room-temperature IL ($T_f = 12$ °C).[336] Although the research community is ambivalent on whether these deep eutectic solvents should be formally classified as ILs for the reason that they contain a significant molecular component, they certainly share a

number of attractive solvent features with regular ILs. The major advantage of this approach is that inexpensive and non-toxic compounds can be used and the properties of the liquid can be finely tuned with different combinations of organic salts and complexing agents. Considering that many inexpensive quaternary ammonium salts are available and there is a wide choice of amides, amines, carboxylic acids, alcohols and metal salts that can be used as complexing agents,[337–341] the possibility of forming new and inexpensive eutectic ILs is enormous. In particular, choline chloride, so called vitamin B$_4$, is produced on the scale of Mtonne (million metric tons) per year as an additive for chicken feed and many other applications. This ammonium salt is not only cheap and easy to make, but also non-toxic and biodegradable. Therefore, eutectic ILs based on cholinium can be biodegradable and inexpensive. In addition, eutectic ILs can dissolve many metal salts, aromatic acids, amino acids, glucose, citric acid, benzoic acid and glycerol.[336, 337, 342–344] Also, choline chloride is an essential micronutrient and human nutrient,[345] and cholinium alkanoates (including acetate) are environmentally benign and biodegradable.[346] One major application of choline-based eutectic ILs is electrodeposition and electropolishing of metals;[342, 347, 348] since this subject has been reviewed for several types of eutectics,[349–351] we will focus on other major applications below.

Abbott et al.[339, 340] reported that quaternary ammonium salts (including choline chloride) mixing with metal halides (such as ZnCl$_2$ and SnCl$_2$) at 1:2 molar ratio could form Lewis acidic ILs, which were further explored as water-insensitive catalysts for Diels–Alder reactions,[352] Fischer indole synthesis,[353] and *O*-acetylation of monosaccharides and cellulose.[354] Recently, the eutectic mixture of choline chloride and zinc chloride (1:2 molar ratio) was used as a Lewis acidic catalyst (Zn$_2$Cl$_5^-$ as predominant species) for the transesterification of soybean oil with methanol, resulting in 52% conversion under optimum conditions (methanol/oil molar ratio 16:1, 10% catalyst, 70 °C and 72 h).[355] A similar transesterification of palm oil catalyzed by choline chloride/ZnCl$_2$ (1:2) or choline chloride/FeCl$_3$ (1:2) along with 95 vol% H$_2$SO$_4$ produced up to 92% methyl ester.[356] However, these eutectic mixtures involving metal halides usually have relatively high freezing points (usually > 25 °C) and very high viscosities (such as 281 Pa s at 25 °C for choline chloride/ZnCl$_2$ at 1:2).[340, 355]

The eutectic mixture of choline chloride and urea in a 1:2 molar ratio has a freezing point of 12 °C,[336] and a fairly high viscosity of ~1200 mPa s at room temperature and 169 mPa s at 40 °C.[338] It has been used as the solvent for the preparation and crystallization of a new coordination polymer Zn(O$_3$PCH$_2$CO$_2$)NH$_4$,[357] (also as template) for the synthesis of zeolite analogues,[358] for the dissolution of poorly soluble compounds (such as benzoic acid, griseofulvin, danazol, itraconazole and an experimental drug AMG517),[359] for freezing-drying incorporation of organic self-assemblies (such as liposomes of ca. 200 nm),[360] and (also as template) for the preparation of aluminophosphates (AlPOs) by the ionothermal method.[361] Mixtures of choline chloride and urea derivatives (such as trifluoroacetamide, 1,3-dimethylurea and 2-imidazolidinone) were used as excellent solvents for the synthesis of vanadium (oxy)fluorides (VOFs).[362] Eutectic ILs, choline chloride/urea (1:2) and choline chloride/ethylene glycol (1:2), were employed as steel/steel contract lubricant, providing a low friction coefficient but suffering some loss short sliding distances.[363] Choline chloride/ethylene glycol (1:2) was used as the electrolyte to determine redox-driven ion transfers accompanying p-doping of polypyrrole (PPy) films;[364] the same eutectic mixture was also used to dissolve MgCl$_2$.[365] However, Yue et al.[366] found that the choline chloride/urea (1:2) mixture exhibited a narrow electrochemical window (< 2.4 V), especially at elevated temperatures, due to electrochemical decomposition of the eutectic mixture. This will likely limit the application of this eutectic mixture in electrochemistry.

Choline iodide/glycerol (1:3, molar ratio) containing 15% water was used as a part of the electrolyte mixture for dye-sensitized solar cells (DSSCs), achieving 3.88% energy conversion efficiency at full sunlight.[367] A 1:1 mixture of quaternary ammonium salt–glycerol was used to extract glycerol from biodiesel product mixtures, and salts including choline chloride, [ClEtMe$_3$N]Cl, and [EtNH$_3$]Cl were found most effective in glycerol removal.[344] The mixture of choline chloride/glycerol (1:1) was found effective in extracting glycerol from biodiesel, resulting in 51 wt% of glycerol removal when the biodiesel/eutectic mixture ratio was kept at 1:1 (molar ratio).[368] In addition, choline chloride/ethylene glycol (1:2.5 molar ratio) and choline chloride/2,2,2-trifluoroacetamide (1:1.75, molar ratio) were shown effective in glycerol removal from palm oil based biodiesel.[369] The Domínguez de María group[370] chose levulinic acid and sugar-based polyols as renewable H-bond donors to form eutectic ILs with choline chloride, and found that the addition of glycerol could reduce the viscous eutectic solvents.

A number of groups have examined the suitability of eutectic ILs as solvents for enzymatic reactions. A study by Gorke et al.[371] has demonstrated the high hydrolase activities in eutectic ILs: several hydrolases (CALB, CALA and epoxide hydrolase) exhibited high activities in eutectic ionic liquids based on choline chloride or ethylammonium chloride (hydrogen-bond donors include acetamide, ethylene glycol, glycerol, urea, and malonic acid). Although some eutectic solvents contain potentially reactive alcohols (such as ethylene glycol or glycerol), ethylene glycol was 9-fold less reactive than 1-butanol, and glycerol was >600-fold less reactive than 1-butanol in CALB-catalyzed transesterifications of butyl valerate. When used as co-solvents, eutectic ILs were capable of improving the reaction rate and/or conversion of hydrolases (esterases and epoxide hydrolase). The polarity study indicated these eutectic solvents are more polar than common imidazolium-based ionic liquids. The H-bond network in eutectic ILs is responsible for reducing the chemical potential of the components of ionic solvents and making them less reactive.

Lindberg et al.[372] investigated the use of eutectic mixtures (choline chloride/ethylene glycol, choline chloride/glycerol and choline chloride/urea, all in 1:2 molar ratio) as co-solvents for the hydrolysis of chiral (1,2)-*trans*-2-methylstyrene oxide catalyzed by potato epoxide hydrolase StEH1; the enzymatic activity decreased with the increasing concentration of eutectic mixtures, however, the reaction media containing eutectic ILs could dissolve ~1.5 times more substrates than the buffer solution and also enhanced the regioselectivity of the reaction. Gutierrez et al.[373] indicated that the choline chloride/glycerol (1:2 molar ratio) mixture preserved the integrity and viability of encapsulated bacteria, implying the possibility of performing whole-cell biocatalysis within eutectic media.

More recently, Zhao et al.[374] developed biocompatible eutectic ILs (such as choline chloride/glycerol at 1:2 and choline acetate/glycerol at 1:1.5) that were capable of maintaining high CALB activity and stability, advocating their promising application in the enzymatic preparation of biodiesel. In addition, those eutectic solvents derived from cholinium salts and glycerol have lower viscosities (~ 80 mPa s at 50 °C) than that of choline chloride/urea 1:2 (120 mPa s at 50 °C).[374] The same group[375] further examined the transesterification activities of cross-linked proteases (subtilisin and α-chymotrypsin), immobilized on chitosan, in these novel eutectic solvents. In the 1:2 molar ratio mixture of choline chloride/glycerol containing 3 vol% water, cross-linked subtilisin exhibited a high activity (2.9 μmol min^{-1} g^{-1}) along with a high selectivity of 98% in the transesterification reaction of *N*-acetyl-l-phenylalanine ethyl ester with 1-propanol. A recent fluorescence and CD spectroscopy study[376] confirmed that α-chymotrypsin was stable in aqueous mixtures of triethylammonium acetate and urea (ratios ranging from 1 M:2 M to 1 M:5 M), due to a reduced protein-urea interaction.

In addition to the use of choline salts in forming eutectic ILs, new mixtures were also reported by mixing protic ammonium salts containing hydroxyl, formyl, thiol and carboxyl groups and urea (or oxalic acid).[377]

8. Toxicity and Biodegradability

Generally, it has been known that the IL toxicity increases with the alkyl chain in the cation, and the cation has a larger impact on the toxicity than the anion.[378–381] The cation toxicity increases in the order of ammonium < pyridinium < imidazolium < triazolium < tetrazolium based on the toxicity of ILs to two aquatic organisms (*Vibrio fischeri* and *Daphnia magna*);[378] however, based on the toxicity towards *Escherichia coli* K-12, imidazolium ILs with short alkyl chains and methylpyrrolidinium ILs are considered relatively non-toxic, whilst water-miscible alkylammonium salts are usually toxic except those containing hydroxyl groups.[382] Pretti et al.[383] indicate that aromatic heterocyclic nitrogen-containing compounds (imidazolium and pyridinium) are more toxic to algae, crustaceans, and fish than non-aromatic cyclic and acyclic compounds (pyrrolidinium, ammonium, morpholinium, sulfonium and thiophenium); however, long-chain quaternary ammonium salts bearing similar structures to surfactants are toxic. Arning et al.[381] suggest that dimethylaminopyridinium, the quinolinium and the pyridinium head groups are more inhibitory to acetylcholinesterase than the polar and nonaromatic morpholinium head group, and the majority of anion species (inorganic, organic and complex borate anions) exhibit no inhibition to acetylcholinesterase except fluoride and fluorine-containing anions (such as PF_6^-) (although another study[140] suggests the F^- concentration released from PF_6^- was too low to be toxic to microorganisms).

In terms of general biodegradability, pyridinium ILs are more biodegradable and environmental benign than imidazoliums,[380, 384] particularly when the cation is functionalized with the ester group and the anion is more degradable (such as octylsulfate).[385, 386] The inclusion of an ester group as a side-chain of the cation usually greatly improve the biodegradability of an IL, however, an amide side-chain often leads to poor biodegradation.[379] Some readily biodegradable anions include octylsulfate,[380] naphthenates,[167] and carboxylates (alkanoates).[346] General reviews on IL's toxicity[387–389] and biodegradation[388–390] have been reported elsewhere. This section will focus on the toxicity and biodegradability of ether/hydroxyl-functionalized ILs with more recent literature updates.

The toxicity of an IL is determined by its most toxic component (cation or anion).[382, 391] For example, imidazolium or quaternary ammonium salts with long alkyl chains are toxic even when pairing with non-toxic saccharinate or acesulfamate anions.[382, 391] A less positively charged nitrogen atom, a more widely delocalized aromatic system, and a lower lipophilicity (or higher polarity) of the cation's side chains are identified as key factors in minimizing the inhibition effect towards acetylcholinesterase.[381] Therefore, the inclusion of a more polar hydroxyl group to the side chain has been shown more effective in reducing the IL's inhibitory effect to acetylcholinesterase than less polar ether and then nitrile groups; hydroxyl-functionalized imidazoliums decreased their inhibition on acetylcholinesterase by one order of magnitude.[381] A similar trend was observed for the lower cytotoxicity against promyelotic leukemia rat cell line IPC-81 for ILs carrying polar hydroxyl, ether or nitrile groups (except the $-CH_2OCH_2CH_3$ group leading to higher cytotoxicity).[392] In general, hydroxyl-functionalized quaternary ammoniums (in particular cholinium salts) and other cations are less toxic or nontoxic,[382, 383] whereas non-toxic anions include alkylsulfates, docusates, alkanoates (carboxylates), lactate, and dimethylphosphate.[382] Various cholinium salts are known having low toxicities, including chloride (*Vibrio fischeri*),[378] saccharinate and acesulfamate (*Daphnia magna*),[165] dimethyl phosphate (*Clostridium sporogenes*),[393] as

well as alkanoates and lactate (*Penicillium brevicompactum, P. glandicola, P. corylophilum, P. diversum*).[346, 394] Wang et al.[395] ranked the cytotoxicity of different ILs against human cell lines HeLa in an increasing order of *N*-alkyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium (choline derivatives) < alkyltriethylammonium < alkylpyridinium < 1-alkyl-3-methylimidazolium, which is in agreement with the previous study[378] and above discussions. Hydroxyl- or ether-functionalization of other cations can also reduce the IL toxicity. Low acute toxicity of 3-hexyloxymethyl-1-methylimidazolium tetrafluoroborate was determined by the Gadumm method, and reported as $LD_{50} = 1400$ mg/kg for female and $LD_{50} = 1370$ for male Wistar rats.[25] The value for acute toxicity of 3-hydroxy-1-octyloxymethylpyridinium chloride was determined as $LD_{50} = 1400$ mg/kg for female and $LD_{50} = 1370$ for male Wistar rats, where LD50 is the dose that is toxic to 50% of the experimental animals. Stasiewicz et al.[396] studied the toxicity of ILs consisting of 1-alkoxymethyl-3-hydroxypyridinium cations and acesulphamate, saccharinate or chloride anions, and suggested the acute biological activity of these compounds was very low in terms of their inhibition of acetylcholinesterase and their cellular toxicity towards the IPC-81 rat promyelocytic leukemia cell line. In examining their cytotoxicity towards two colon carcinoma HT-29 and CaCo-2 cell lines, hydroxyl/ether-functionalized imidazoliums were found less toxic than alkyl-substituted analogues, and the overall cytotoxicity was labeled in an increasing order of cholinium < hydroxyl/ether-imidazolium < alkylimidazolium < tetra-*n*-hexyldimethylguanidinium < tri-*n*-hexyl-*n*-tetradecylphosphonium < tri-*n*-octylmethylammonium (Aliquat).[397] Another study also confirmed that imidazolium ILs bearing monoethoxy and diethoxy chains exhibited lower toxicity than the alkyl-substituted IL ([BMIM]Cl) in inhibiting the growth and photosynthetic efficiency of two algal species (*Skeletonema marinoi* and *Phaeodactylum tricornutum*).[398] This is consistent with the correlation of a higher IL lipophilicity leading to a higher cytotoxicity[388, 392, 399] with some exceptions [such as more polar 4-(dimethylamino)pyridinium being more cytotoxic[392]]. A more comprehensive comparison of IL cytotoxicity in terms of their inhibition of Leukemia Rat Cell Line IPC-81 and acetylcholinesterase (AChE) (see Table 3 in Ref[388] and Table A1 in Ref[400]) suggests that ether/hydroxyl-functionalized ammoniums, imidazoliums, morpholiniums, piperidiniums, pyridiniums, and pyrrolidiniums are less cytotoxic than alkyl-substituted counterparts in general (with some exceptions). Furthermore, the inclusion of ether groups into the ester side-chains of imidazolium ILs considerably reduced the toxicity compared with alkyl ester derivatives.[401] In inhibiting the growth of an anaerobic bacterium, *Clostridium* sp. by 1-methoxyethyl-3-methyl imidazolium based ILs ([MeOEt-MIM]$^+$), [MeOEt-MIM][BF$_4$] was noticed less toxic than [BMIM][BF$_4$]; in addition, the anion's ability in inhibiting the bacterial growth was found in a decreasing order of $Tf_2N^- \geq PF_6^- > BF_4^- > CF_3COO^- >$ OMs$^-$ (methane sulfonate), which corresponds to the reducing number of fluorine atoms in these anions.[402] When comparing with non-functionalized imidazolium ILs, Deng et al.[141] suggest that the ether and ester-functionalized ILs are more water soluble, but diffuse more slowly in water (due to heavier and larger cations); as a result, these functionalized ILs are less toxic to four bacteria (*Bacillus cereus* ATCC 14579 and *Rhodococcus rhodochrous* ATCC 29672 as Gram positive bacteria, *Pseudomonas aeruginosa* ATCC 17504 and *Escherichia coli* ATCC 11303 as Gram negative ones) and one yeast (*Candida albicans* CIP444).

The introduction of oxygen atoms to the IL substituents often lead to a lower IL thermal stability, but this also makes the IL more susceptible to biodegradation and hydrolysis.[73] Generally, pyridinium salts are known not reacting with ozone under aqueous conditions, however, 1-alkoxymethyl-3-hydroxypyridinium and 1-alkoxymethyl-3-dimethylaminopyridinium chlorides were reported reacting with ozone in aqueous solution indicating their high biodegradability; the biodegradability of 3-hydroxy-1-octyloxymethylpyridinium chloride was found to be 80% within 24 d (according to OECD

303 A).[36] Stasiewicz et al.[396] indicated the biodegradability of ILs consisting of 1-alkoxymethyl-3-hydroxypyridinium cations and acesulphamate, saccharinate or chloride anions ranging from 21% to 72%, and the incorporation of ether and hydroxyl groups to the cation is believed to increase the biodegradation rate. Cholinium salts, such as most naphthenates (closed-bottle test, OECD 301D) (except that choline 2-naphthoxyacetate [Ch][NOA] and choline anthracene-9-carboxylate [Ch][AC] failed the degradation test)[167] and alkanoates (*Penicillium corylophilum*),[346] are more biodegradable than ILs carrying aromatic cations. Attaching an ester group to the side chain of imidazolium cation has proven to improve its biodegradability based on the CO_2 headspace test (ISO 14593).[403, 404] However, the inclusion of a hydroxyl group to the side chain showed no improvement in biodegradation; on the other hand, paring imidazolium cations with alkylsulfate, lactate or saccharinate anions leads to higher IL biodegradability.[404] On the contrary, Stolte et al.[405] observed no significant biological degradation of imidazolium ILs with short alkyl (≤C6) and short functionalized side chains (ether, hydroxyl, nitrile, and carboxylic acid). Another study[406] also suggests phosphonium cations containing ester, ether, alcohol and alkene functionality have poor biodegradability based on the CO_2 headspace test (ISO 14593), although ester-functionalized phosphoniums coupled with octylsulfate anion result in up to 30% biodegradation in 28 days (at least 60% is considered readily biodegradable). Deng et al.[141] indicate that the incorporation of an ether group to the cation is rather a disadvantageous to biodegradation; the inclusion of ester group to the imidazolium cation often leads to fast hydrolysis under abiotic and biotic conditions, however, the resulting products are more difficult to further biodegrade due to the poor biodegradation and abiotic degradation of imidazolium ring itself.

9. Summary

In general, the ether-functionalization of an IL induces a lower melting point and lower viscosity, while the hydroxyl-functionalization increases its viscosity. Both functionalizations increase the polarity, hydrophilicity and hydrogen-bonding capability of the resulting IL, at the price of lower thermal stability. The ether- and hydroxyl-functionalization typically reduces the toxicity of ILs, but does not have a significant impact the biodegradability of ILs; the ester group in side chain can induce a higher biodegradation, but the ultimate IL biodegradability depends on the core of cation (such as imidazolium ring) and anion (such as octylsulfate). As the alkoxy chain can be designed in different lengths and shapes, such a functionalization can truly allow a fine tuning of ILs' physicochemical properties for particular applications. We enthusiastically foresee that there will be more research on the designing of this type of functionalized ILs, as well as further development of their applications in a variety of areas.

Acknowledgments

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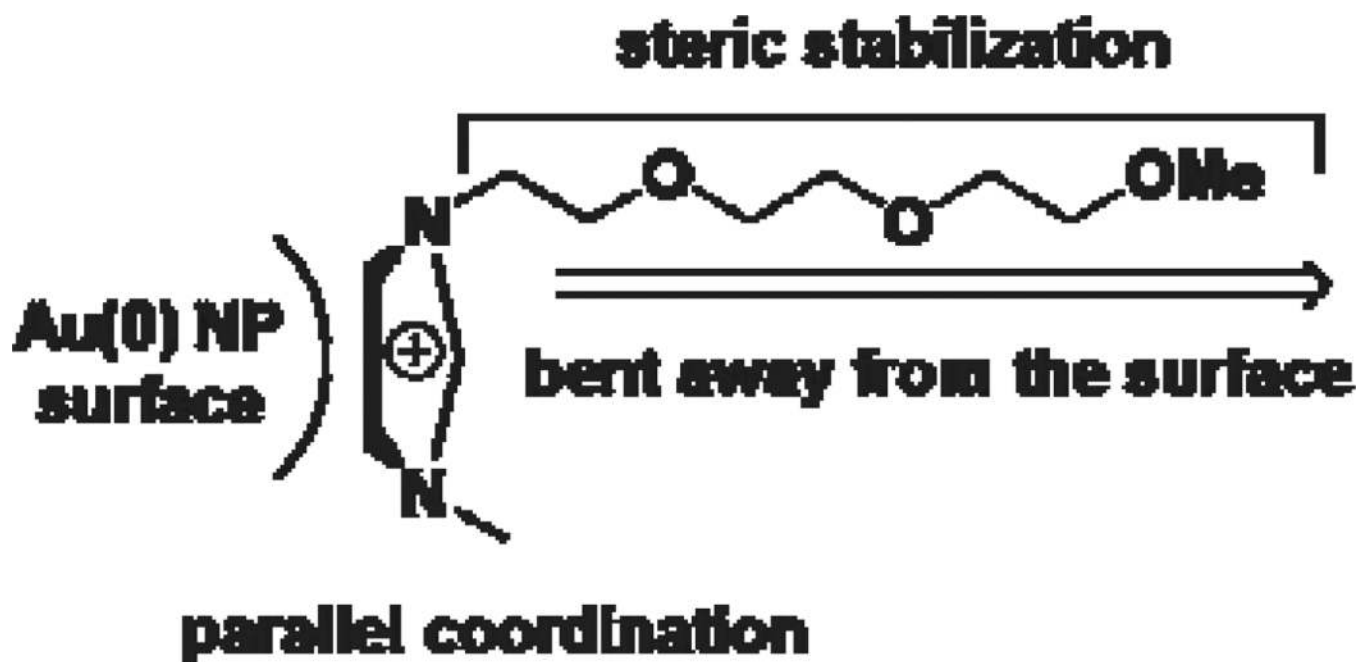
Figure 1.
Stabilization mode of ether-functionalized imidazolium ILs (adapted from ref,[302] reproduced with permission of Elsevier B.V.).
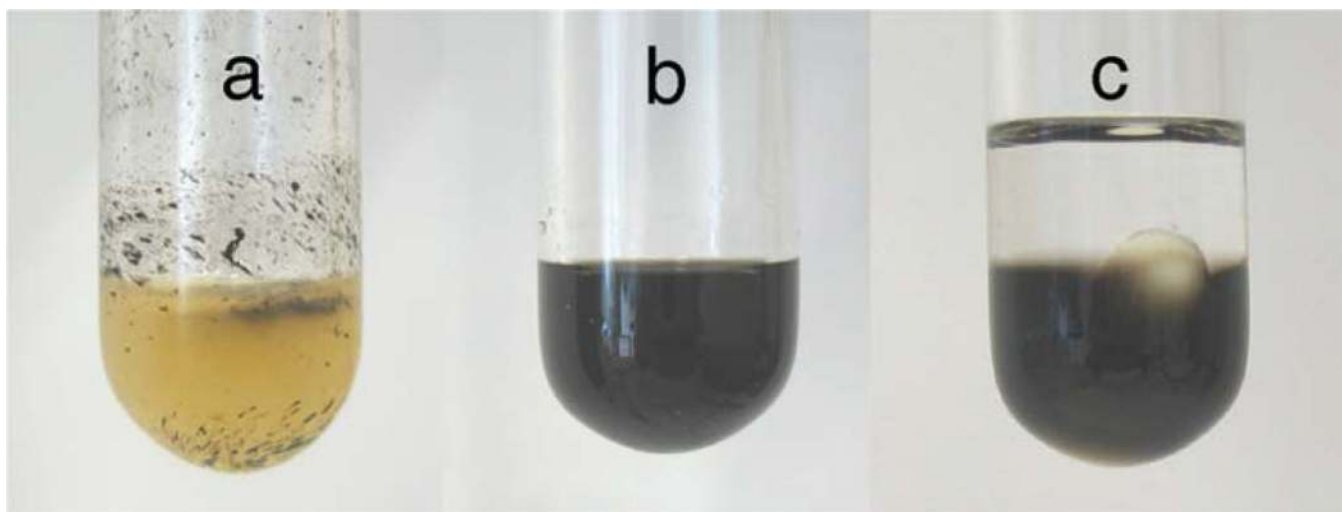
Figure 2.
Photographs of Rh nanoparticles dispersed in (a) [C$_2$mim][BF$_4$], (b) [C$_2$OHmim][BF$_4$], and (c) [C$_2$OHmim][BF$_4$] after hydrogenation of styrene (Reprinted with permission from Ref.[303] Copyright 2008 American Chemical Society).
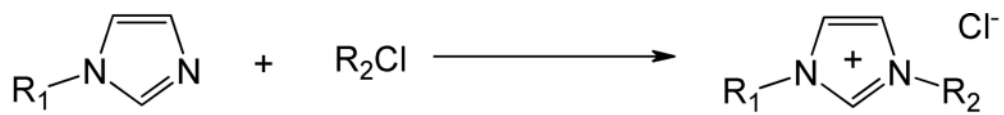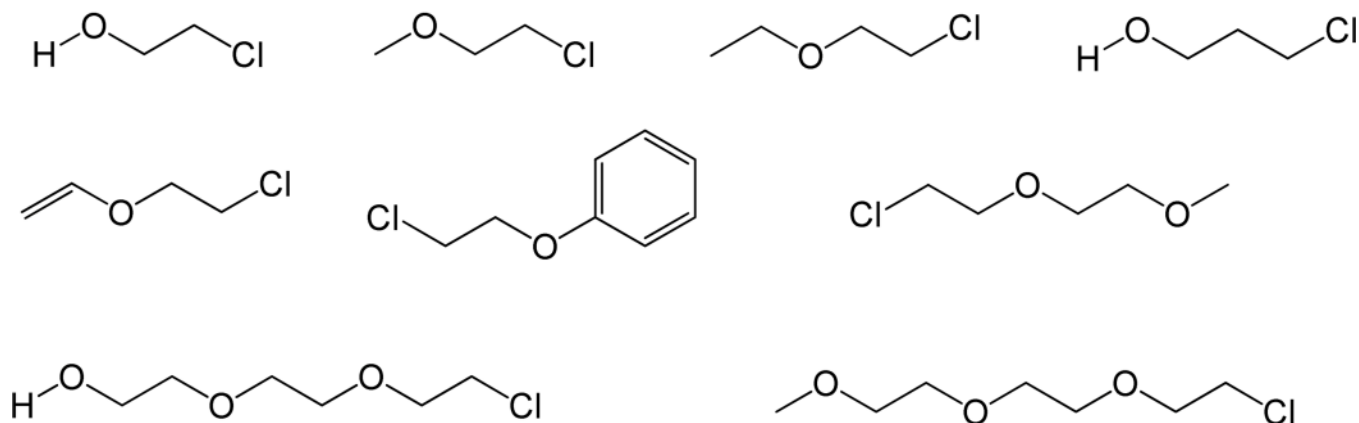
Scheme 1.
Quaternization of alkylimidazole using oxygen-containing alkyl halides.
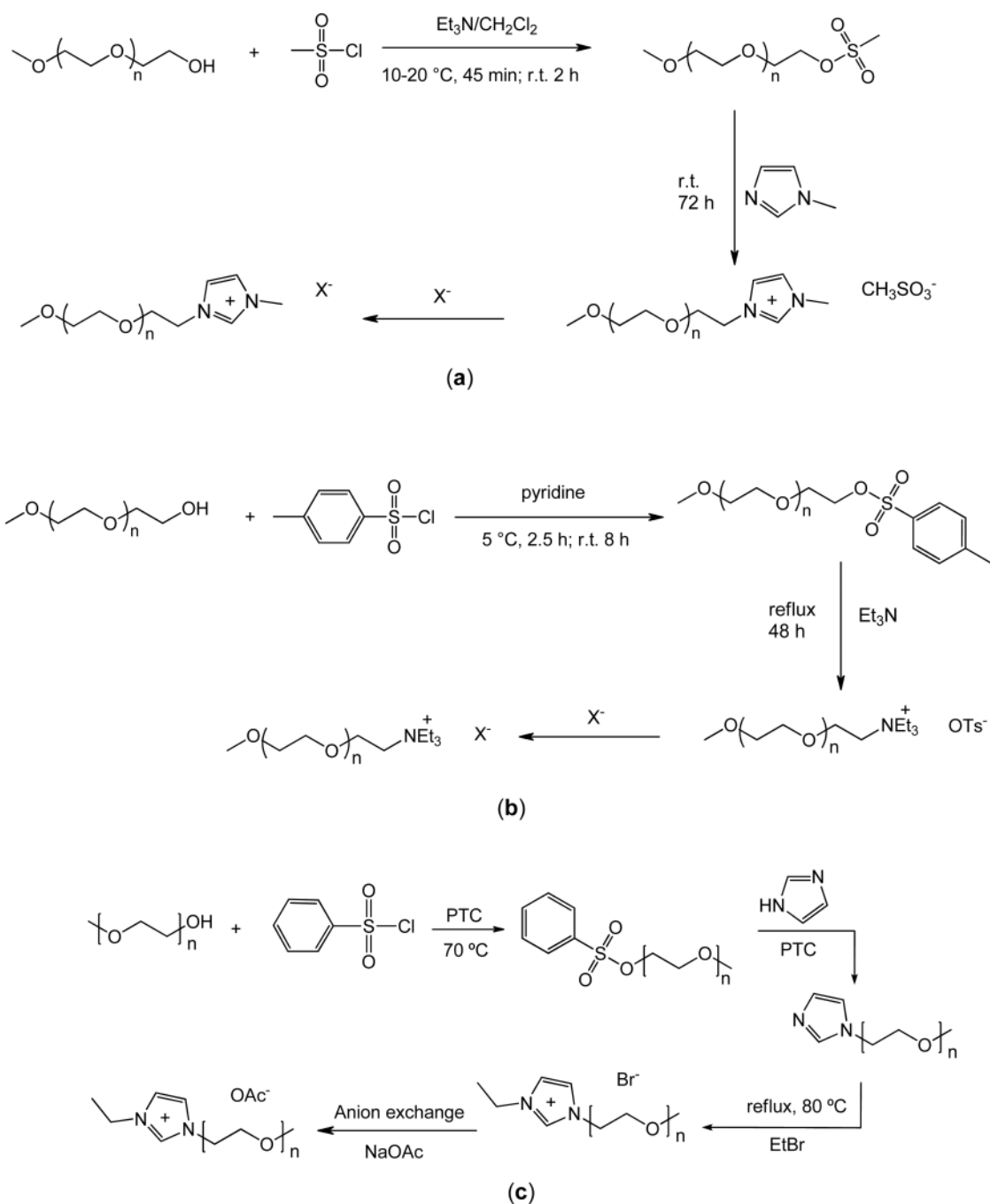
Scheme 2.
Ether-functionalization of onium ions through sulfonation and quaternization using (a) methanesulfonyl chloride[34, 61, 62] (or similar reagents[63]); (b) *p*-toluenesulfonyl chloride;[64–66] and (c) benzenesulfonyl chloride.[31, 67]
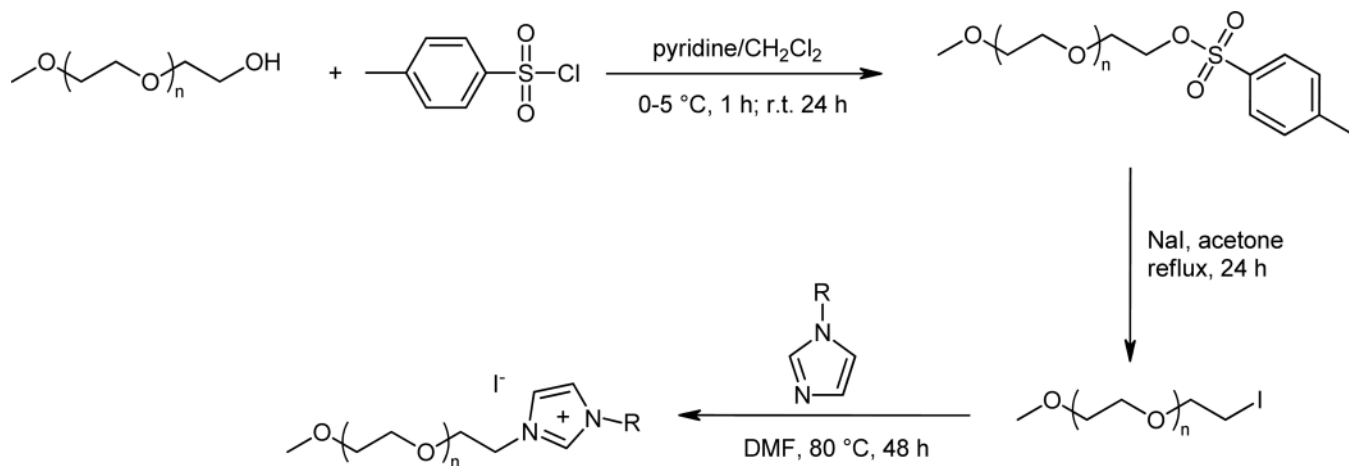
Scheme 3.
Synthesis of methoxy-terminated PEGylated imidazoliums.
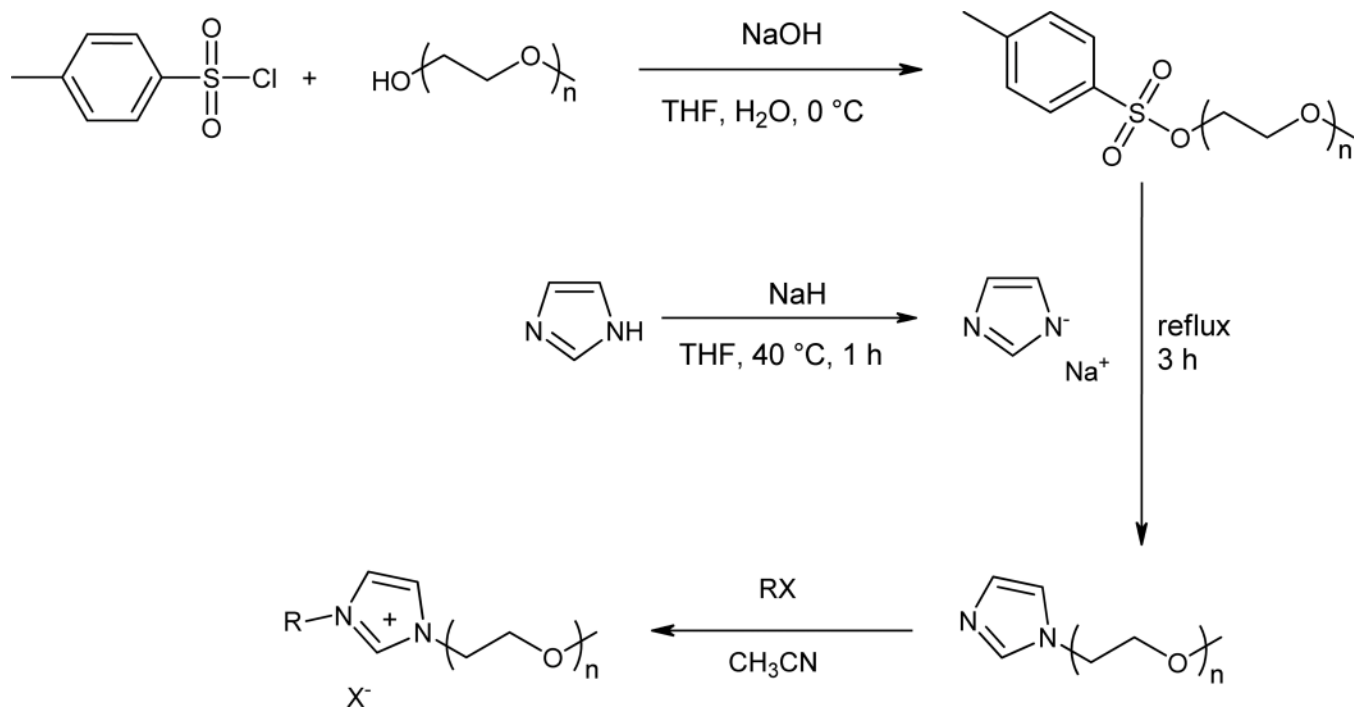
Scheme 4.
Preparation of ether-functionalized imidazolium salts *via* tosylation and subsequent alkylation.
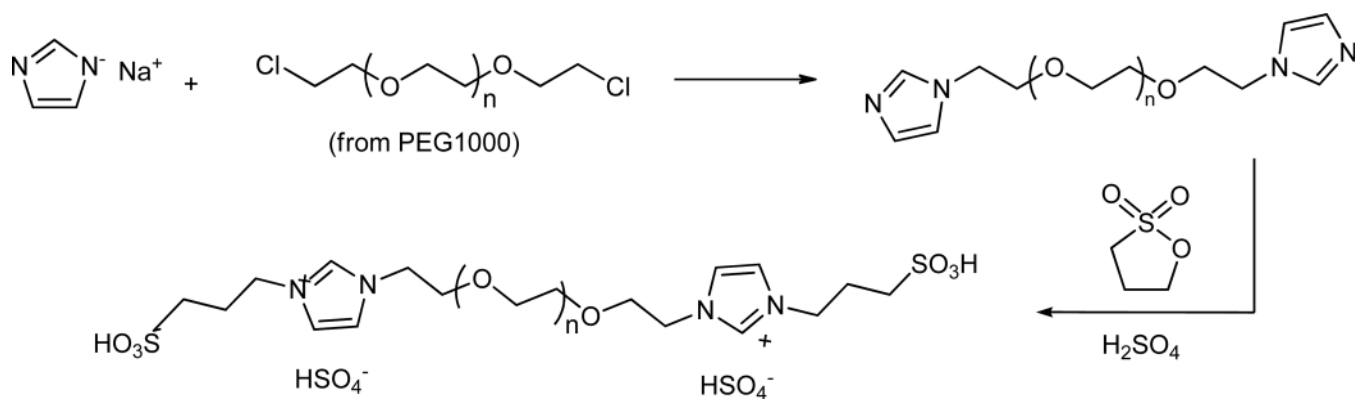
Scheme 5.
Synthesis of PEG-1000-based geminal di-imidazolium Brønsted acidic ILs.
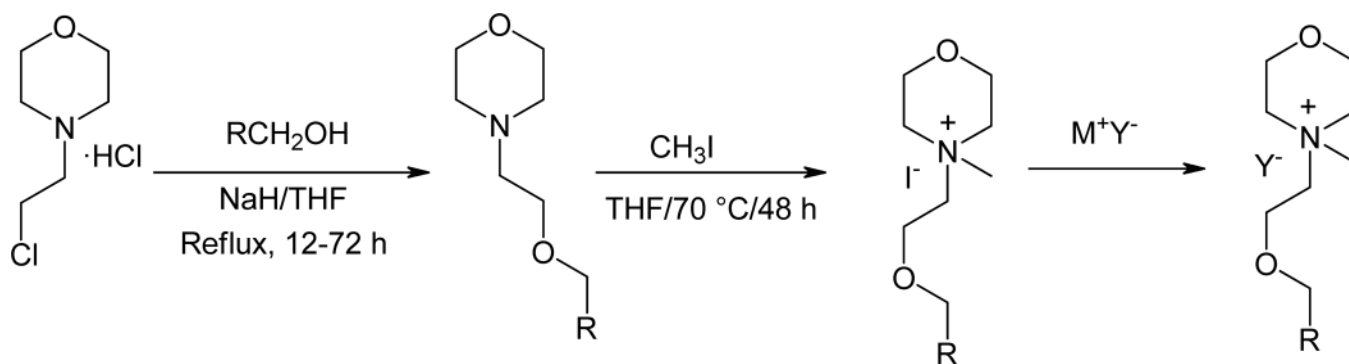
Scheme 6.
Grafting of an alkoxyl group through etherification.
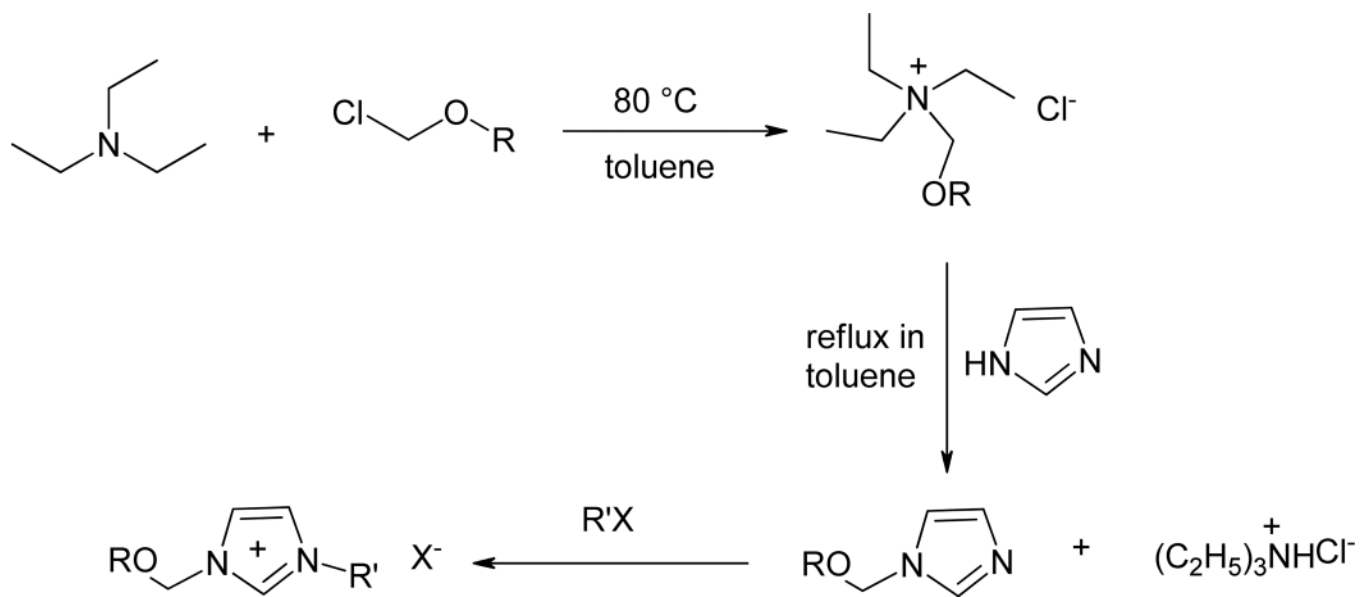
Scheme 7.
N-Alkoxymethylation of imidazole to yield an ether-decorated imidazolium salt.
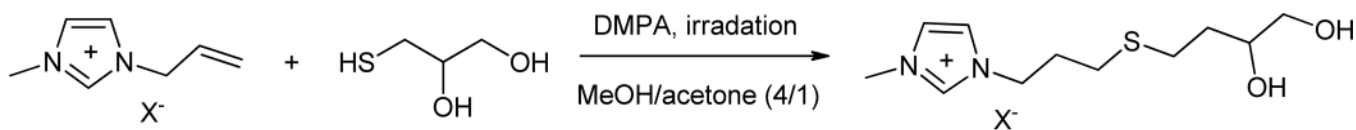
X = Cl, Br, or Tf$_2$N

Scheme 8.
Thiol–ene "click" chemistry preparation of a thioether appended cation.
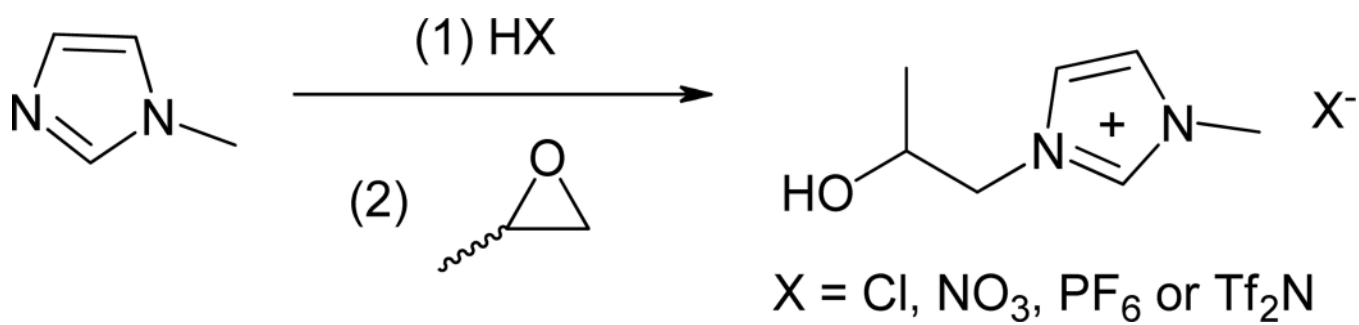
Scheme 9.
One-pot synthesis of 1-(2-hydroxypropyl)-3-methylimidazolium ILs using propylene oxide.
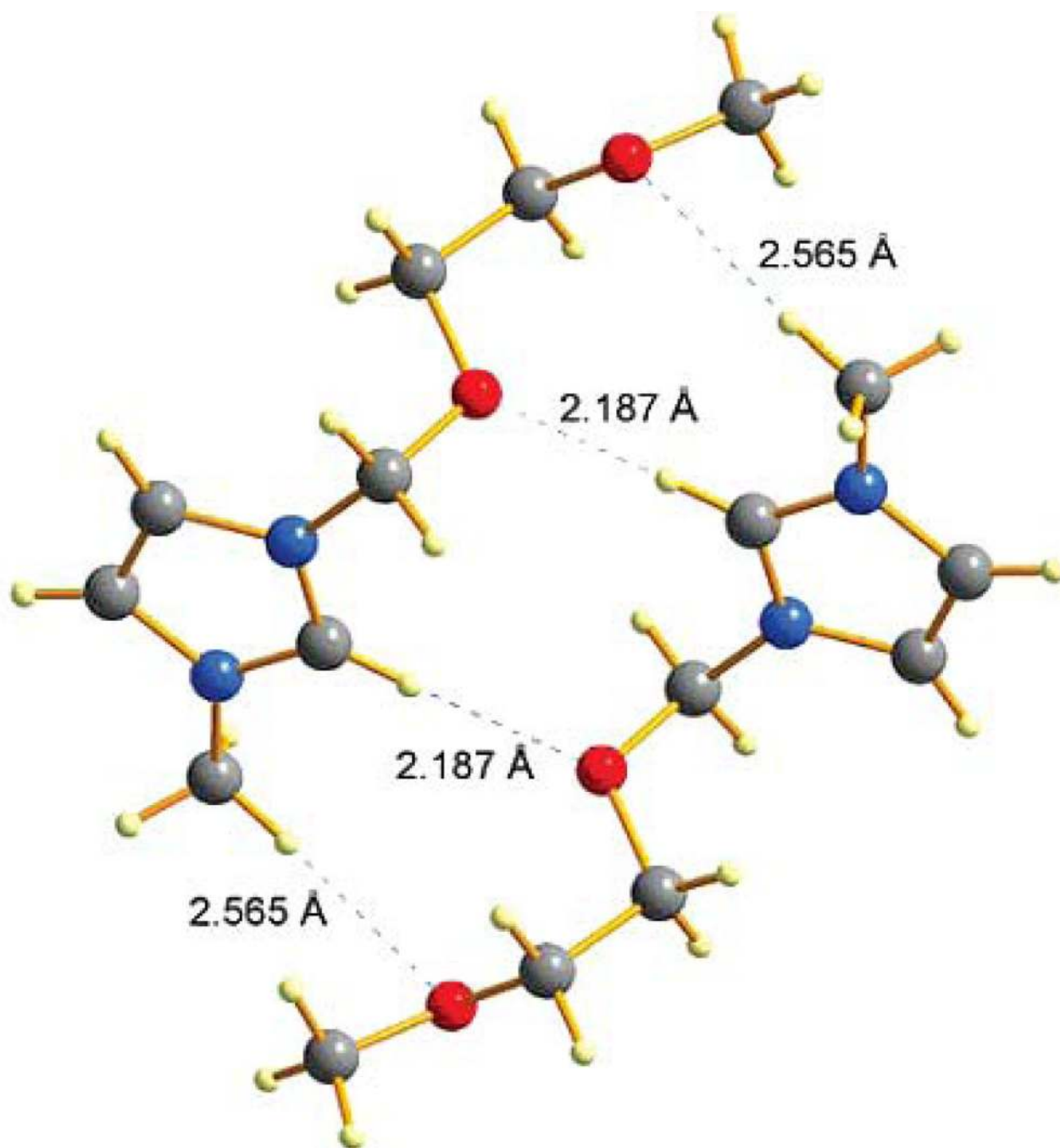
Scheme 10.
Illustration of intermolecular hydrogen-boning in [CH$_3$O(CH$_2$)$_2$OCH$_2$-MIM]I. Atoms are shown in spheres with arbitrary radii. Iodide anions and disordered atoms are omitted for clarity (Reprinted with permission from Ref.[125] Copyright 2007 American Chemical Society).

(a)

R = CH$_3$ or CF$_3$

(b)

Br$^-$

(c)

Br$^-$ Br$^-$

(d)

SO$_3^-$ Li$^+$ Li$^+$ $^-$O$_3$S

(e)   Li$^+$ $^-$O$_3$S   SO$_3^-$ Li$^+$
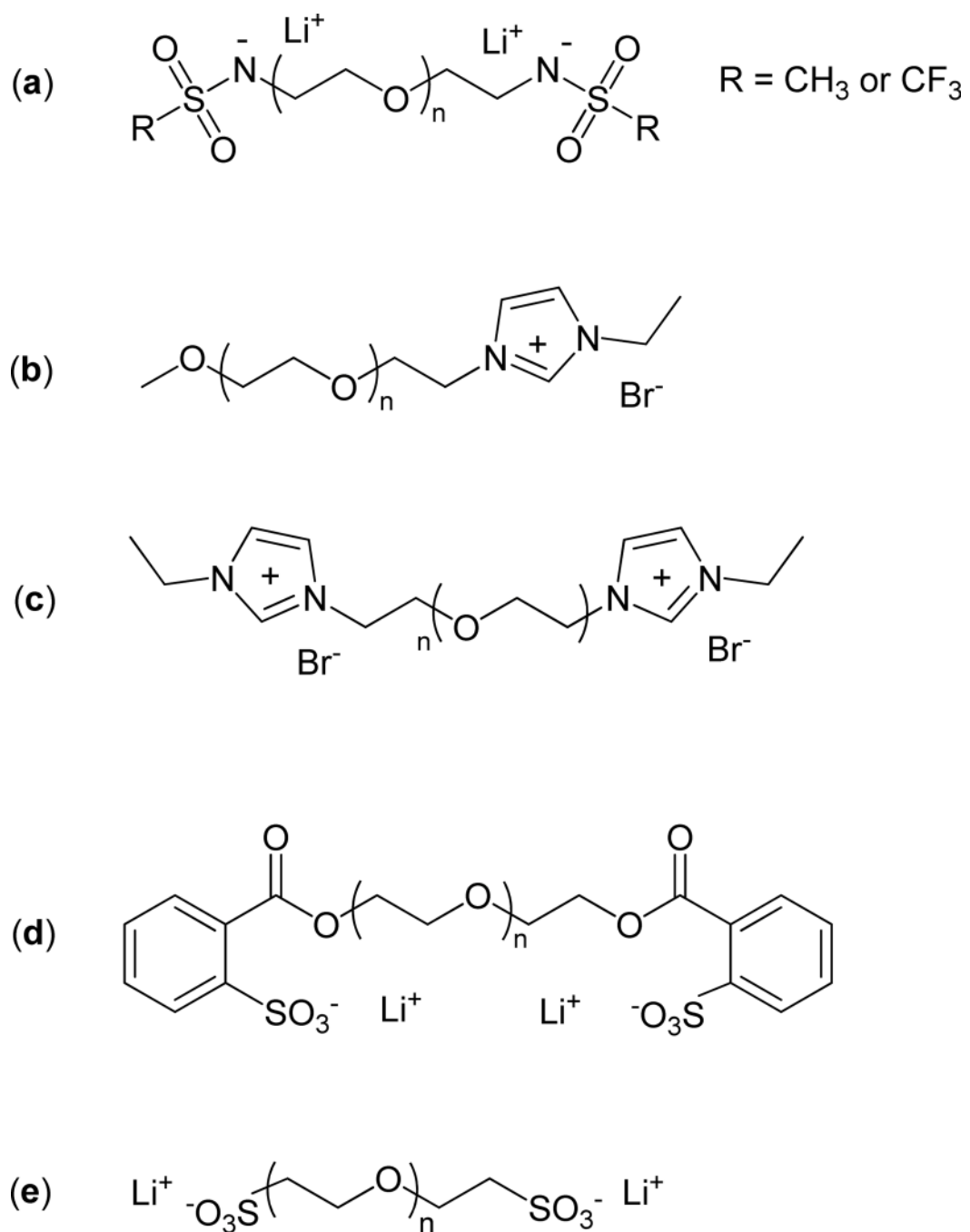
Scheme 11.
PEG-derived liquid ionic polymers.
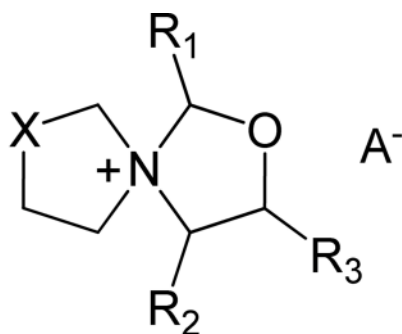
$X = CH_2$ or O

$R_1 = H$, Me or Et

$R_2 = H$ or Me

$R_3 = H$ or Me

$A = BF_4$, $BF_3C_2F_5$, Tf_2N

Scheme 12.
Modified ether-functionalized spirobipyrrolidinium salts.
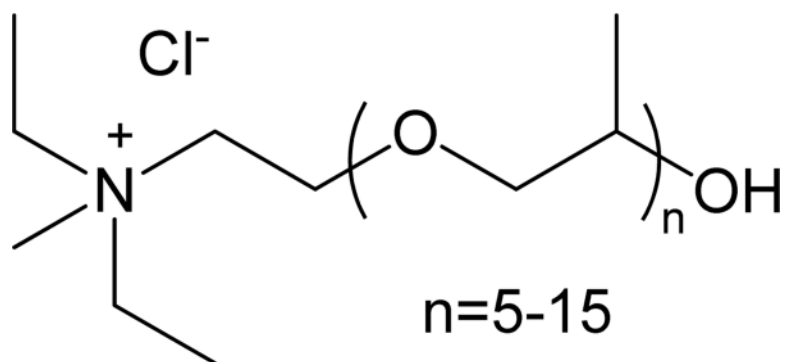
Scheme 13.
Structure of Ammoeng 110.
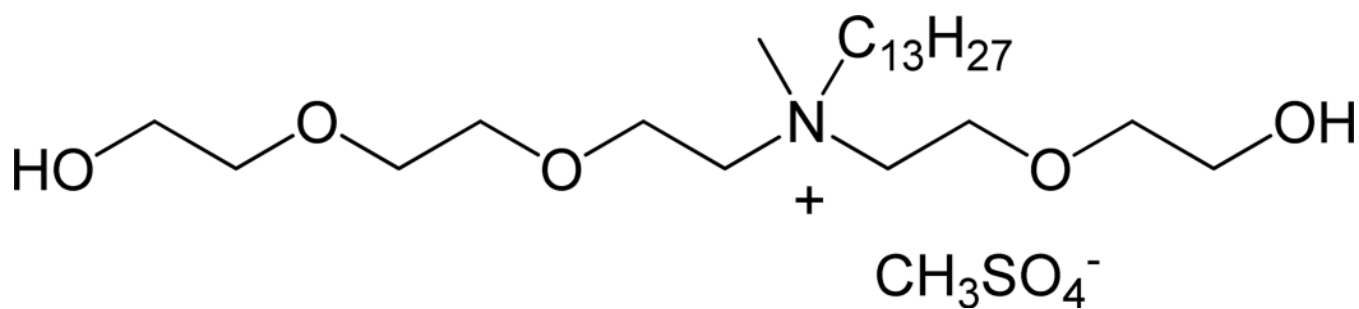
Scheme 14.
Structure of PEG-5 cocomonium methylsulfate (Ecoeng 500).

$$CO_2 + MEA + H_2O \rightleftharpoons HCO_3^- + MEAH^+ \quad (1)$$

$$HCO_3^- + MEA \rightleftharpoons MEACO_2^- + H_2O \quad (2)$$

$$CO_2 + 2\,MEA \rightleftharpoons MEACO_2^- + MEAH^+ \quad (3)$$
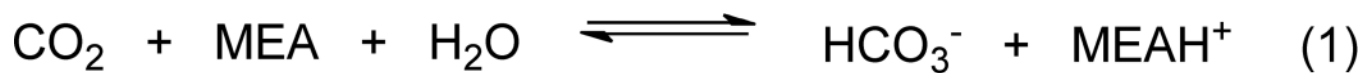
Scheme 15.
Chemical absorption of CO_2 using aqueous alkanolamines.

$R = -(CH_2)_6-$ or $-(CH_2)_2-O-(CH_2)_2-$, or $-((CH_2)_2-O)_2-(CH_2)_2-$
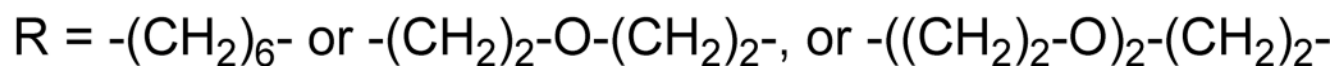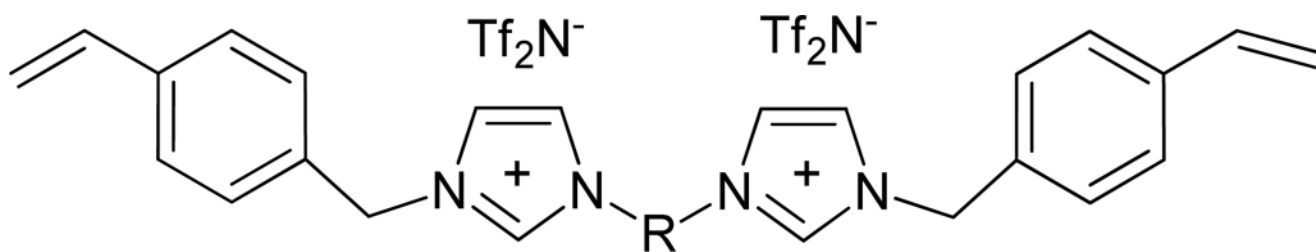
Scheme 16.
Preparation of polymerizable Gemini ILs.
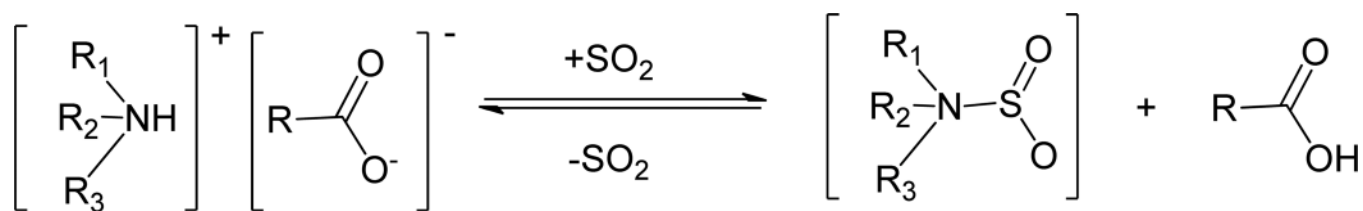
R1, R2, R3 = H, CH$_3$, or HO-CH$_2$CH$_2$-

R = H, CH$_3$, or CH$_3$CH(OH)-

Scheme 17.
Proposed reversible reaction between hydroxyl ammonium ILs and SO$_2$.

Scheme 18.
Imidazolium and ammonium based ILs consisting of alkyloxyalkyl-substituted cation and acetate anion (abbreviated as [CH$_3$(OCH$_2$CH$_2$)$_n$-Et-Im][OAc] and [CH$_3$(OCH$_2$CH$_2$)$_n$-Et$_3$N] [OAc] respectively) (n = 2, 3,…).
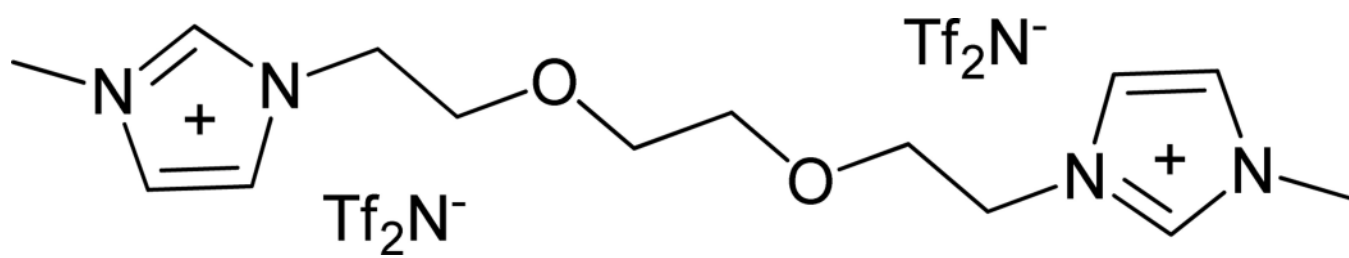
Scheme 19.
Ether-functionalized dicationic IL.

$$R = C_2H_5, \ C_3H_7, \ldots, \ or \ C_{12}H_{25}$$
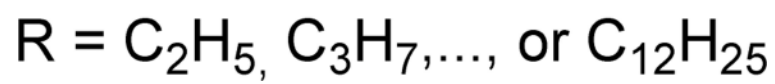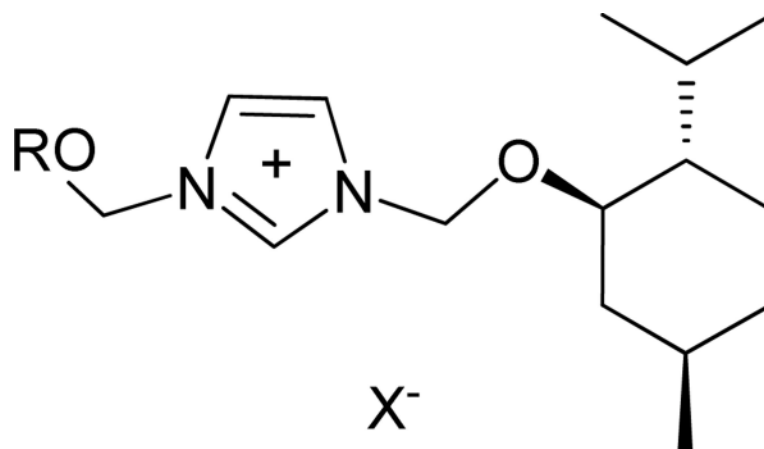
Scheme 20.
Ether-functionalized ILs based on menthoxymethylimidazolium.
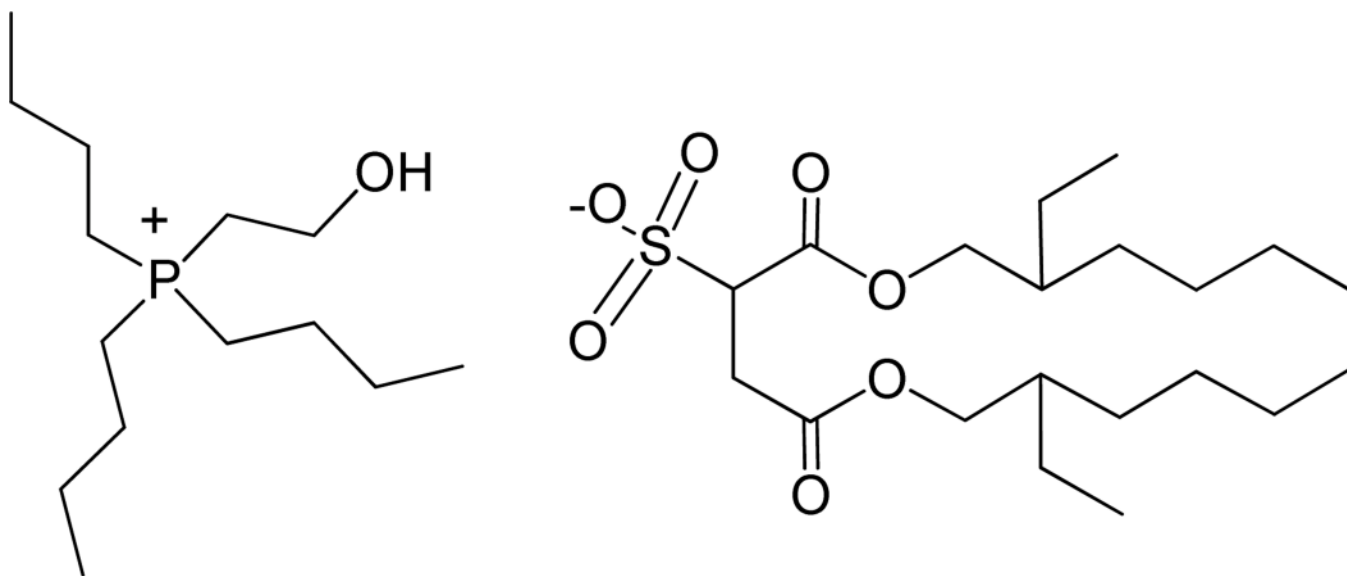
Scheme 21.
Structure of tributyl(2-hydroxyethyl)phosphonium bis(2-ethylhexyl)sulfosuccinate (docusate).
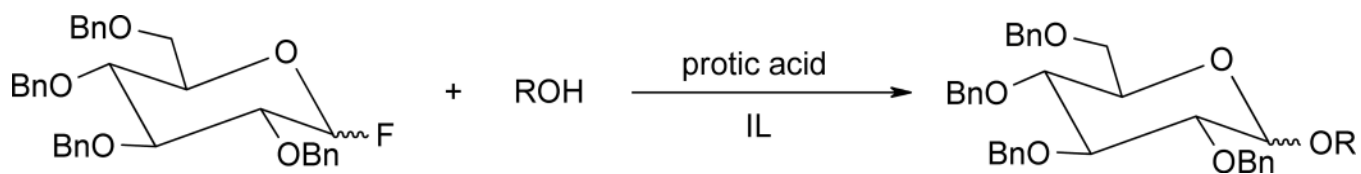
Scheme 22.
Protic acid-catalyzed glycosidation of glycosyl fluoride with an alcohol in an IL.
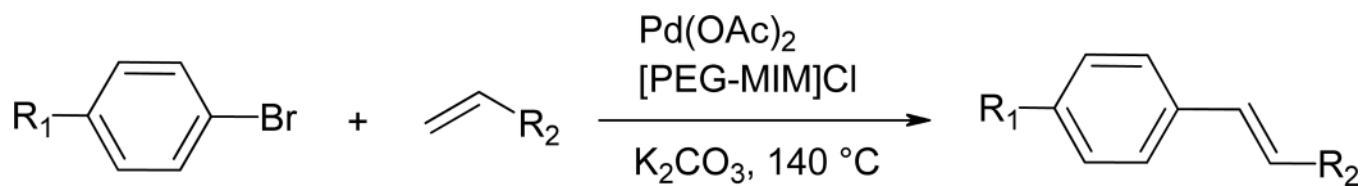
Scheme 23.
Heck reaction of bromoarene with olefin catalyzed by Pd(OAc)$_2$ in a PEGylated IL.
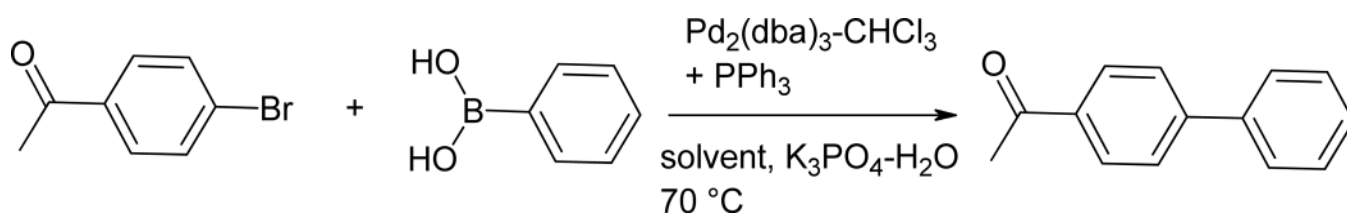
Scheme 24.
Suzuki cross-coupling of phenylboronic acid and 4-bromoacetophenone.
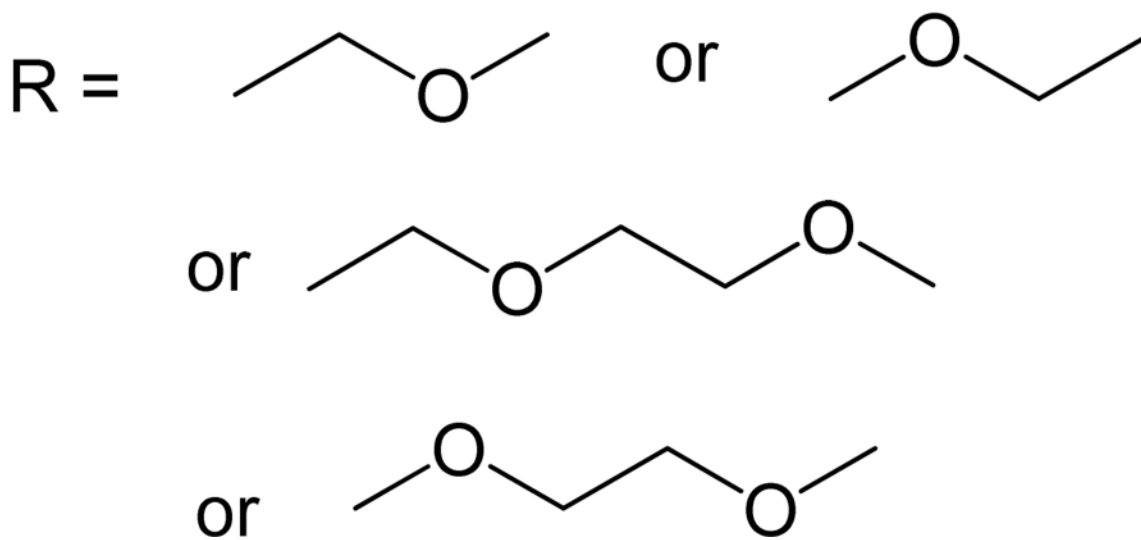
Scheme 25.
Structures of ether-grafted imidazolium and pyridinium ILs for Suzuki coupling.
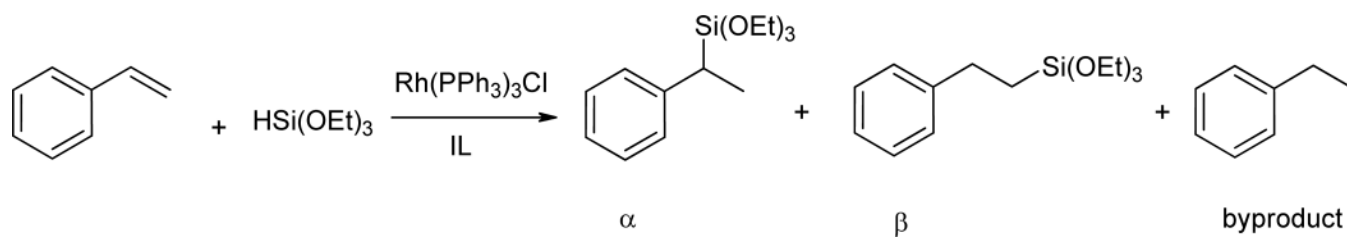
Scheme 26.
Hydrosilylation of styrene with triethoxysilane.
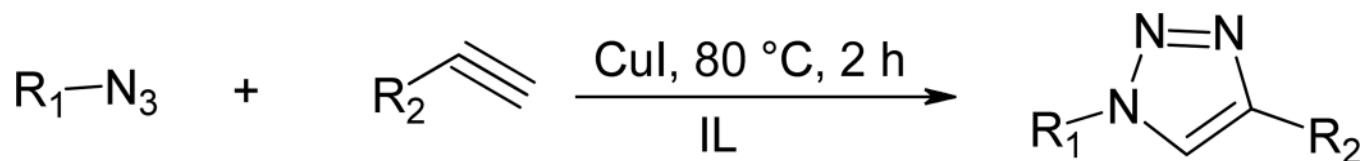
Scheme 27.
CuI-catalyzed azide-alkyne cycloaddition (CuAAC).
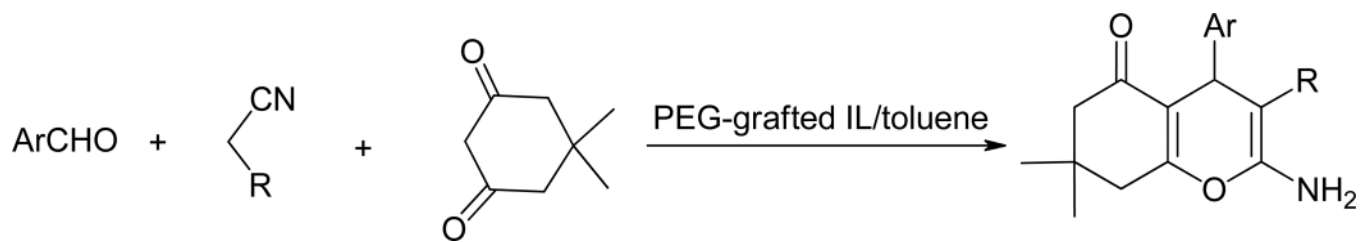
Scheme 28.
One-pot synthesis of benzopyrans.
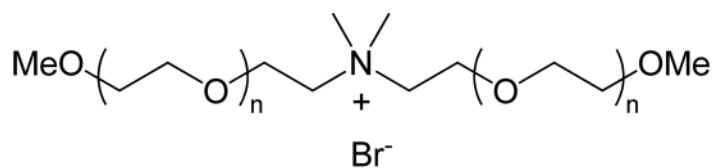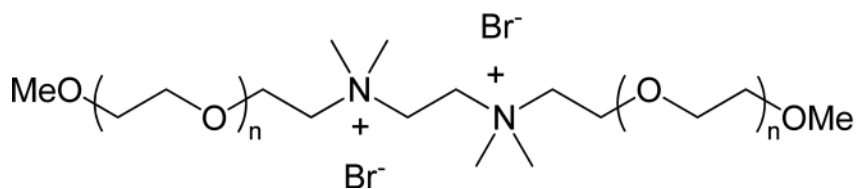
Scheme 29.
Two bis-PEG-350-functionalized ILs.
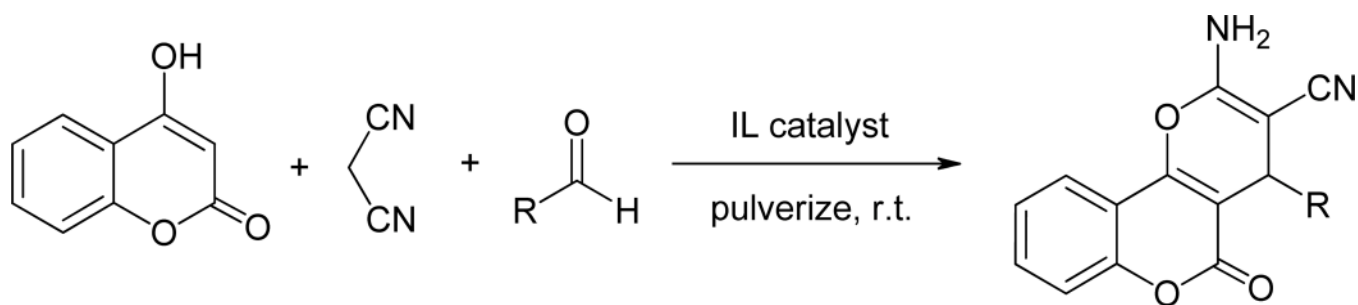
Scheme 30.
Hydroxyl-functionalized IL-catalyzed synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives.
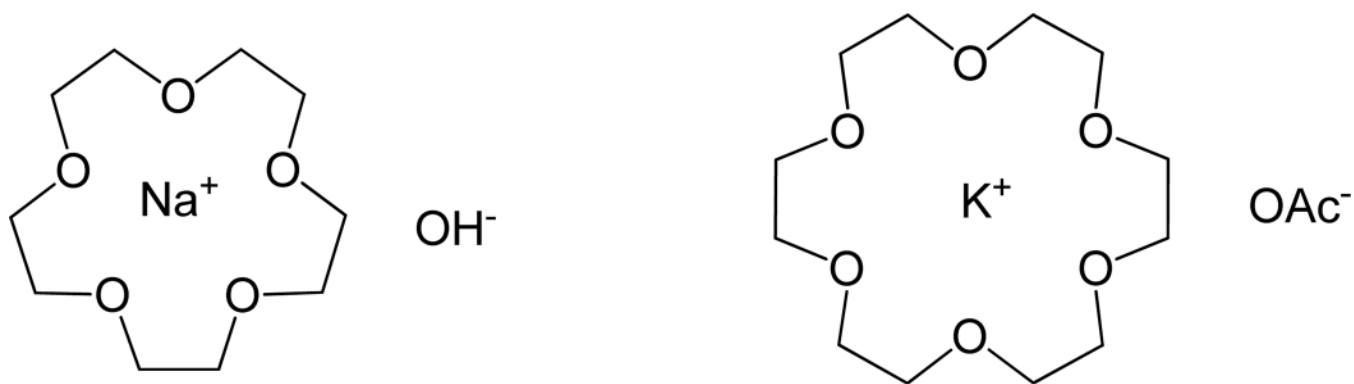
Scheme 31.
Structures of [15-C-5Na][OH] and [18-C-6K][OAc] (15-C-5 = [15]-crown-5; 18-C-6 = [18]-crown-6).
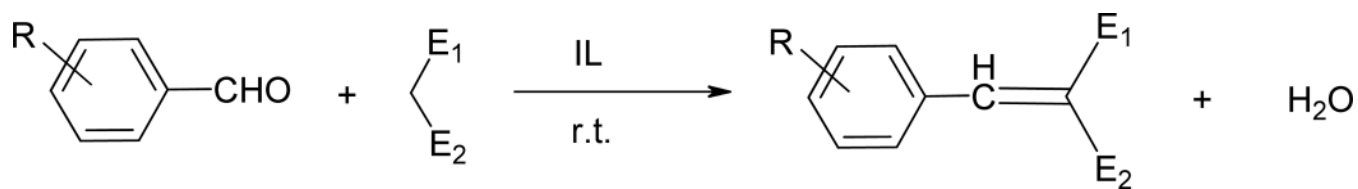
Scheme 32.
Knoevenagel condensation of aromatic aldehydes with activated methylene compounds.
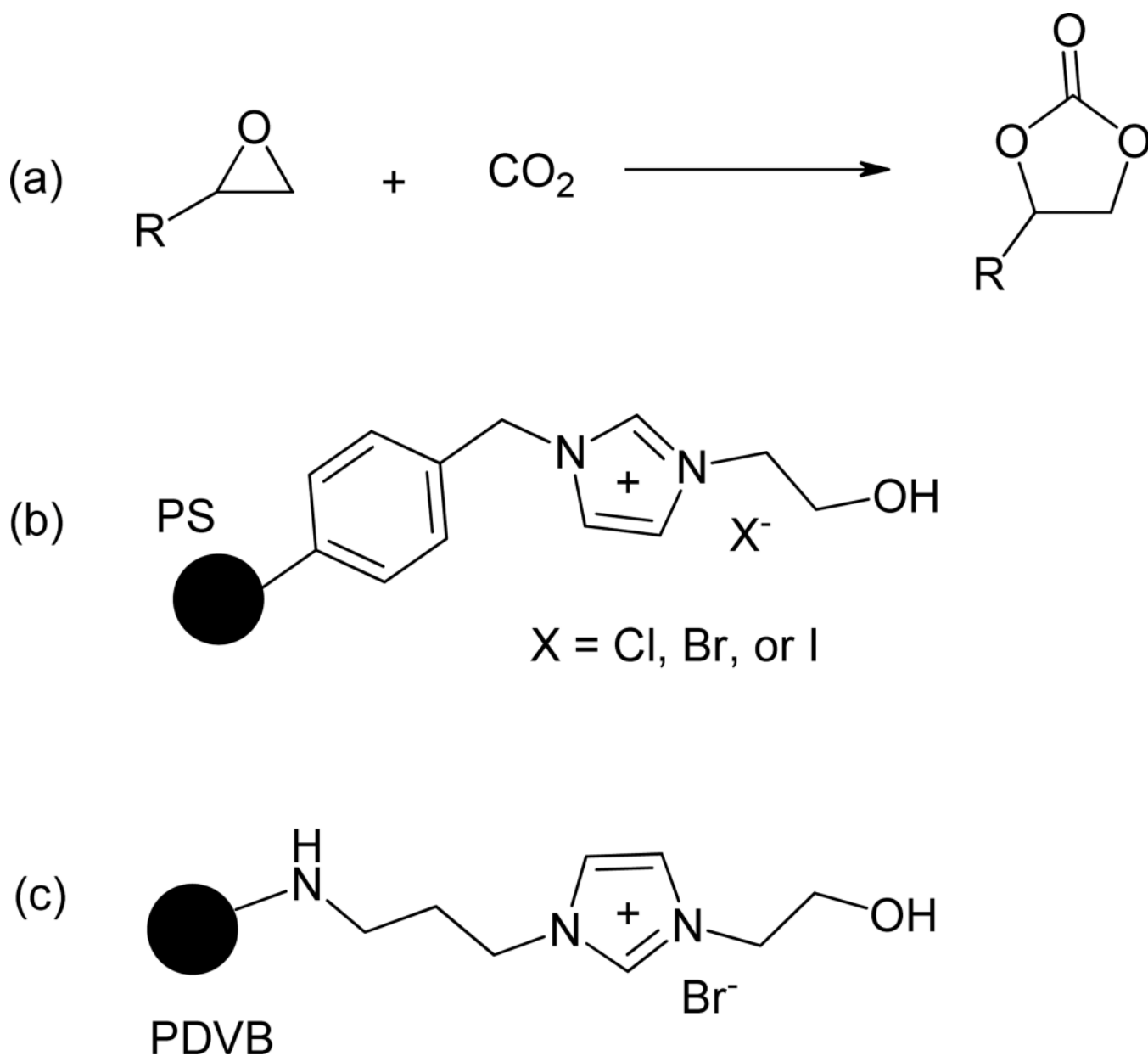
Scheme 33.
(a) Synthesis of cyclic carbonates using a cycloaddition reaction between an epoxide and CO_2. Hydroxyl-containing imidazolium ILs covalently attached to (b) highly cross-linked chloromethylated polystyrene (PS),[254] and (c) cross-linked poly(divinylbenzene) (PDVB) polymer beads.[255]
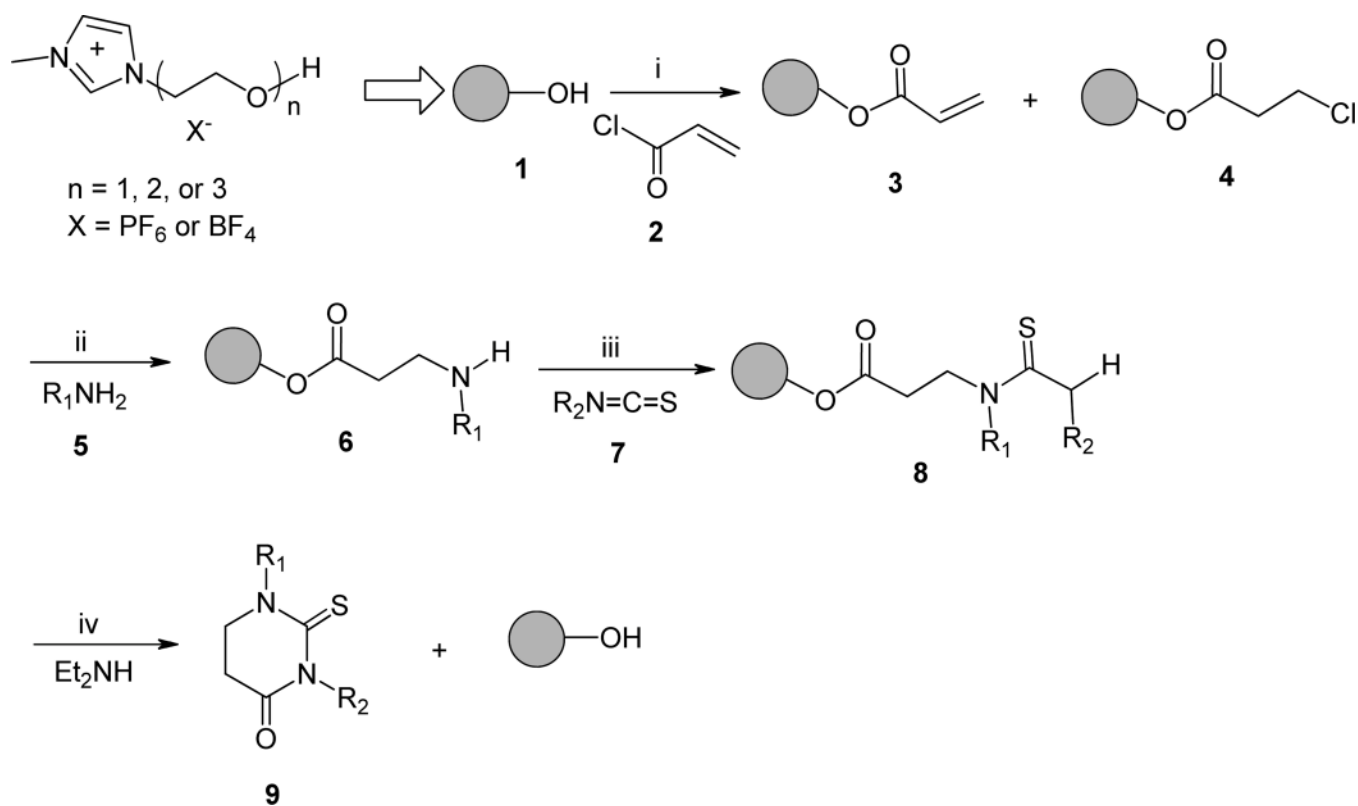
Scheme 34.
IL phase organic synthesis (IoLiPOS) of 2-thioxo tetrahydropyrimidin-4-(1*H*)-ones.
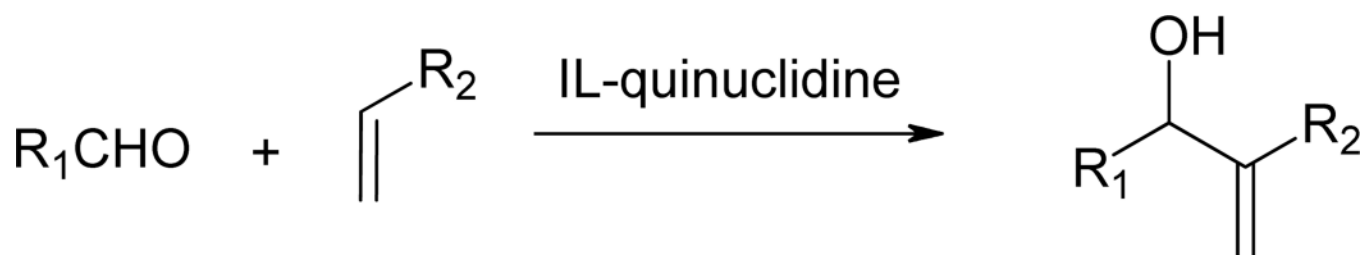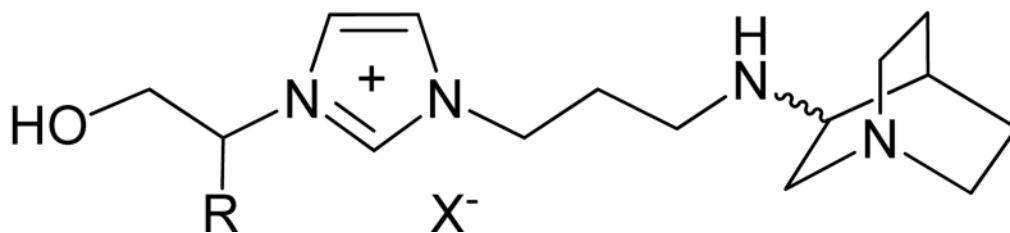
Scheme 35.
Baylis–Hillman reaction catalyzed by IL-supported quinuclidine.
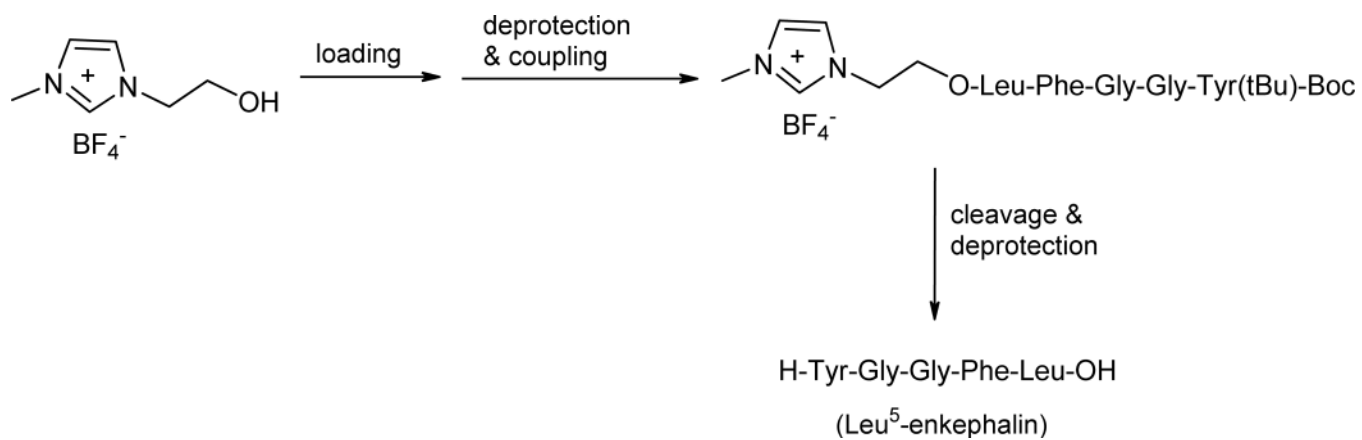
Scheme 36.
IL-supported peptide synthesis.
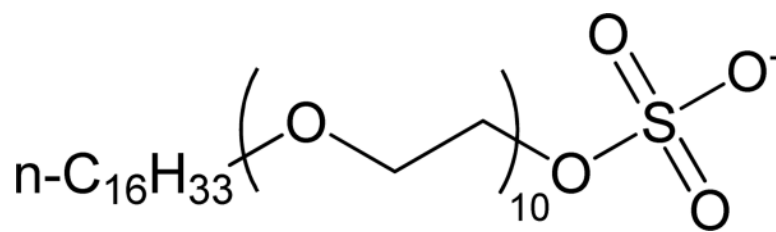
Scheme 37.
Structure of polyoxyethylene(10) cetyl sulfate.
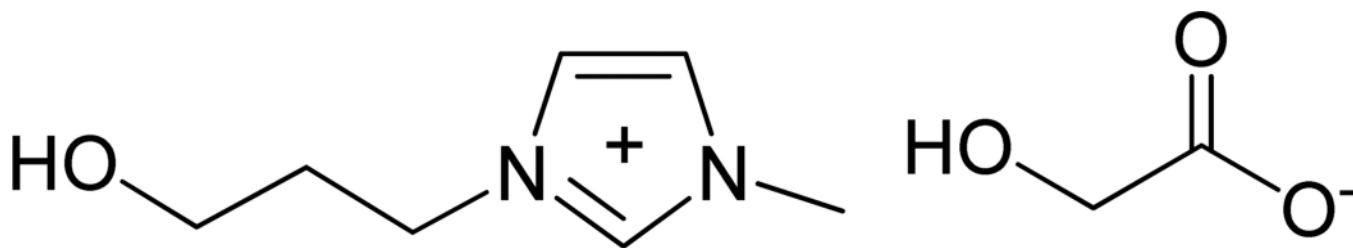
Scheme 38.
Structure of 1-(3-hydroxypropyl)-3-methylimidazolium glycolate.
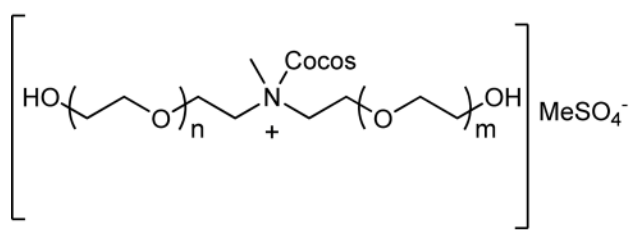
(a) Ammoeng 100

Cocos, C_{14} alkyl group; m + n =4-14
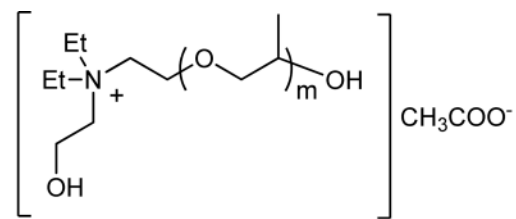
(b) Ammoeng 111

m = 50-60
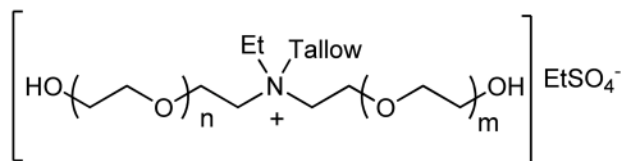
(c) Ammoeng 102

Tallow, C_{18} acyl group; m + n =14-25
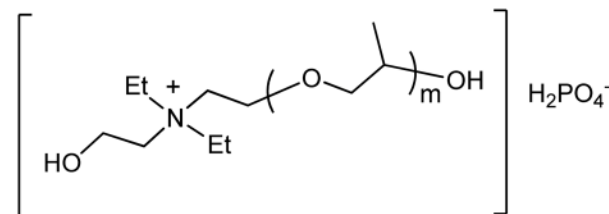
(d) Ammoeng 112

m = 50-60
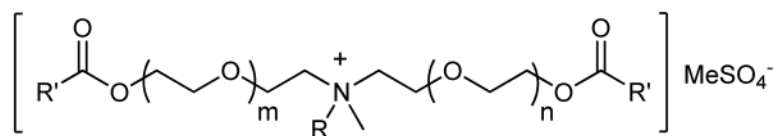
(e) Ammoeng 120

R, R', C_{18} acyl group; m, n, unavailable

Scheme 39.
Structures of tetraammonium-based ILs (Ammoeng series).
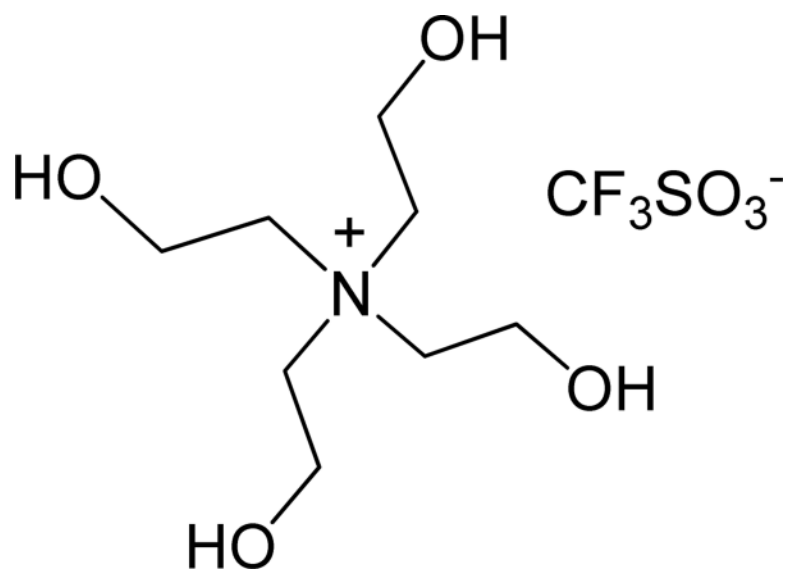
Scheme 40.
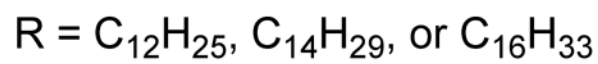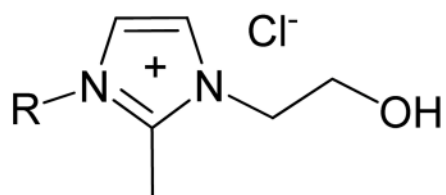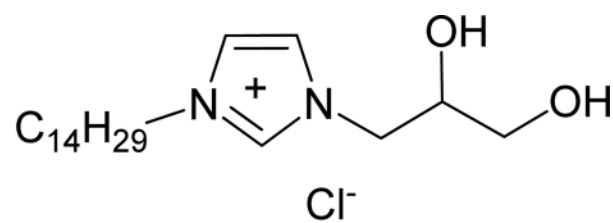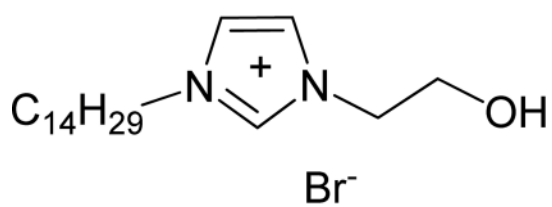Structure of tetrakis(2-hydroxyethyl)ammonium triflouromethanesulfonate.
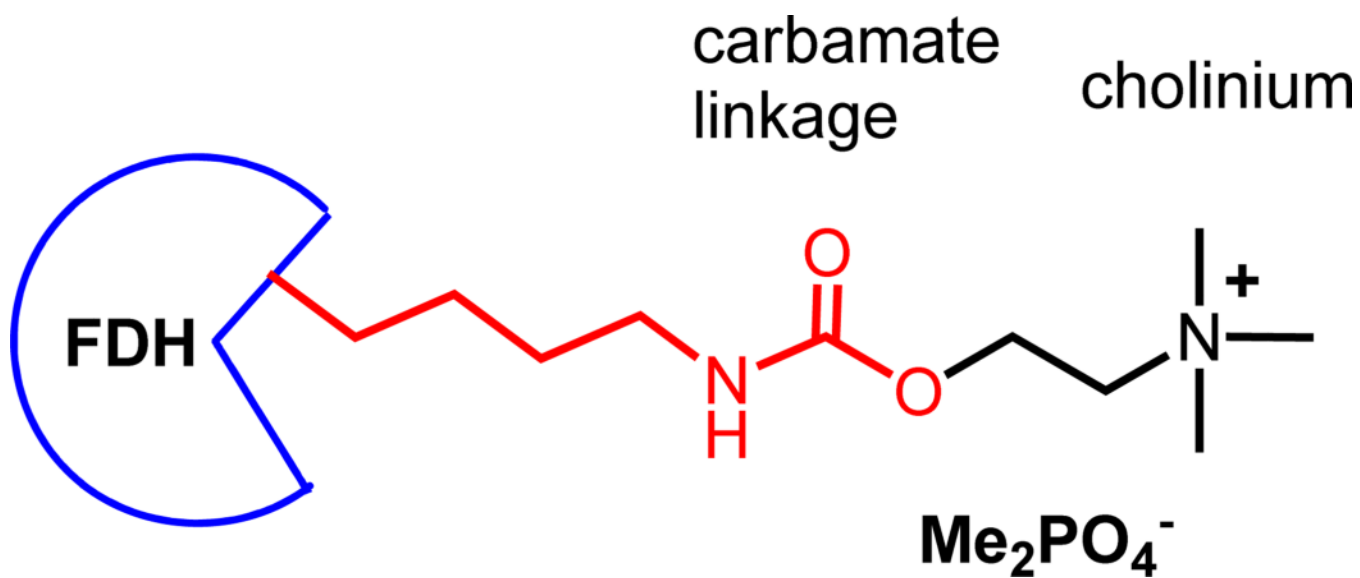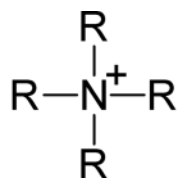
Scheme 41.
Covalent attachment of a cholinium salt to the lysine residue of FDH.
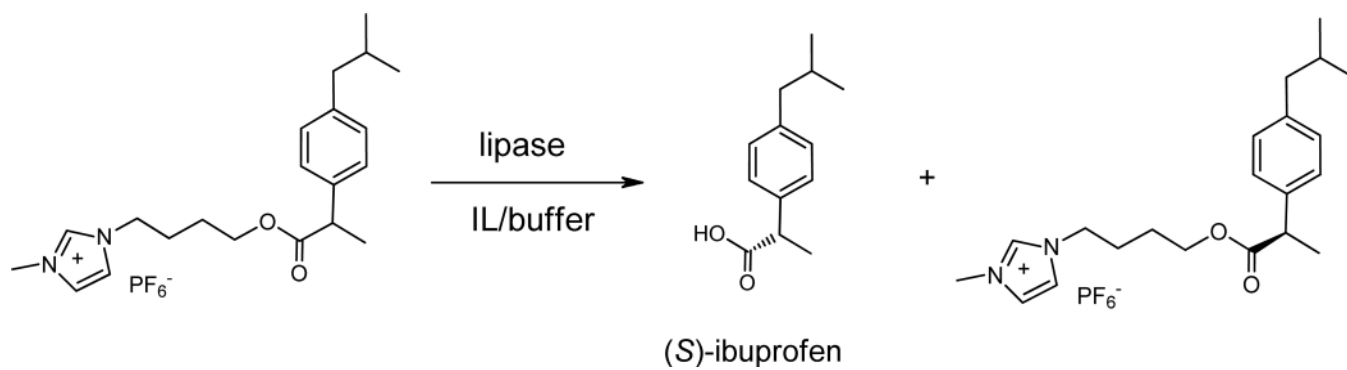
Scheme 42.
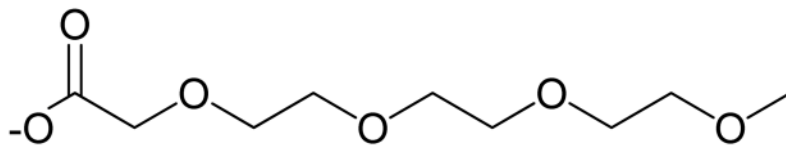Lipase-catalyzed kinetic resolution of IL-anchored ibuprofen ester.

Scheme 43.
Structures of hydroxyl-functionalized ILs and surfactants.

R = ethyl, propyl or butyl

or
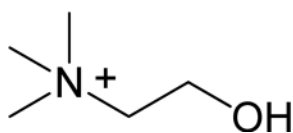
Scheme 44.
Quaternary ammonium salts of oligoether carboxylate.
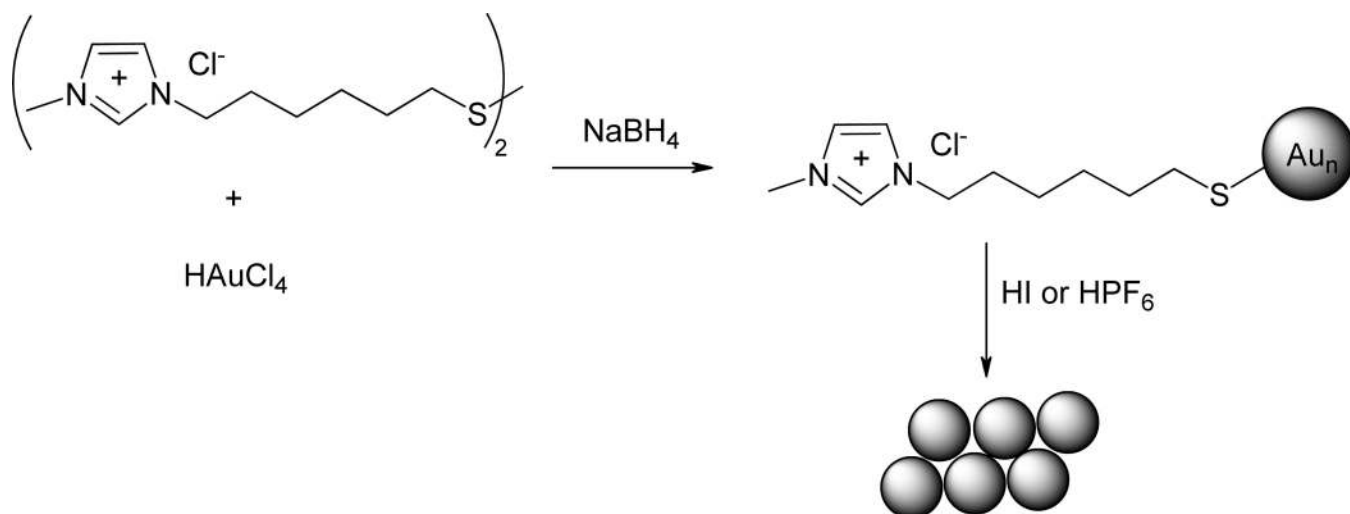
Scheme 45.
Au NP stabilization using a thiol-functionalized IL.
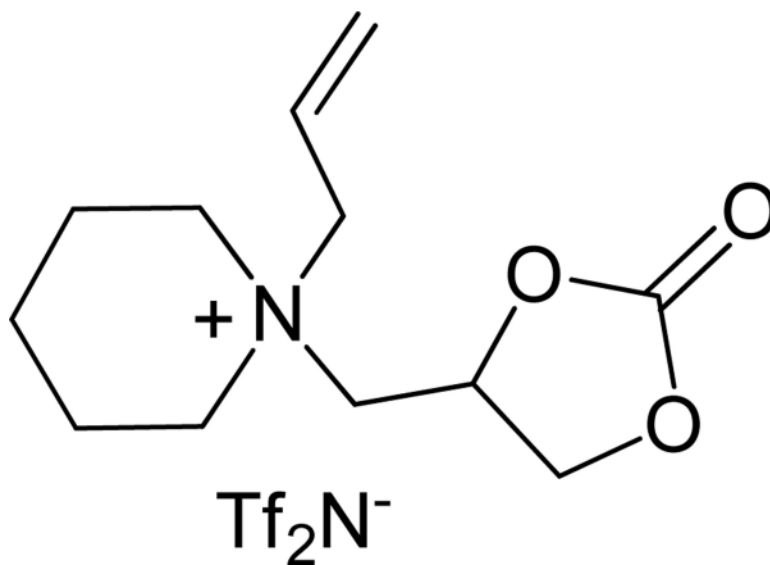
Scheme 46.
Propylene carbonate-functionalized piperidinium RTIL.
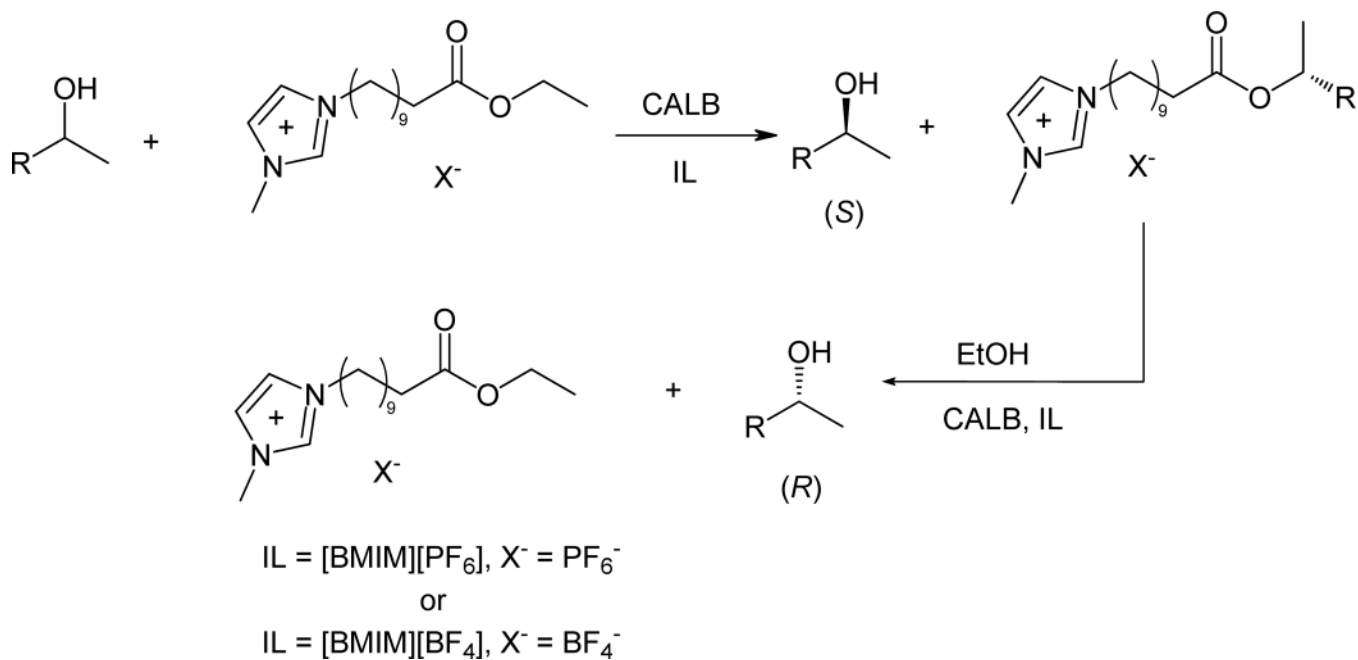
Scheme 47.
One-pot enzymatic resolution and separation of *sec*-alcohols using ionic acylating agents in ILs.
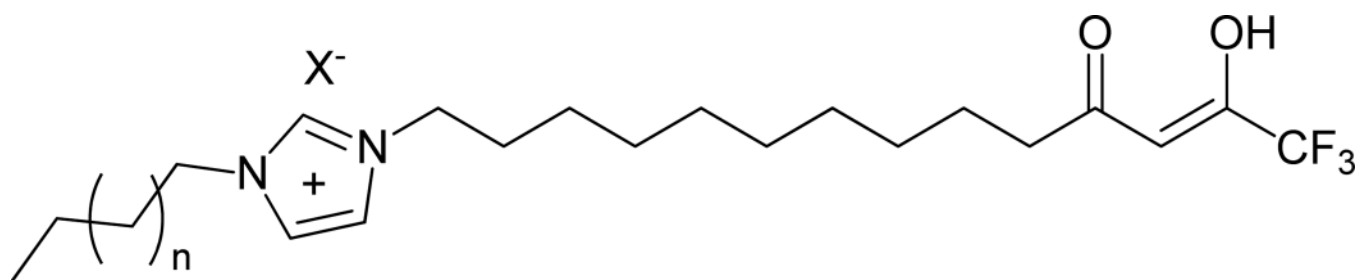
n = 1, 5, 9, or 13

X = BF$_4$, PF$_6$, or Tf$_2$N

Scheme 48.
Diketonate-functionalized RTILs.

Scheme 49.
Structures of cholinium salts (choline chloride and choline acetate).

Table 1

Viscosity comparison between aliphatic side-chain ILs and oxygen-functionalized versions

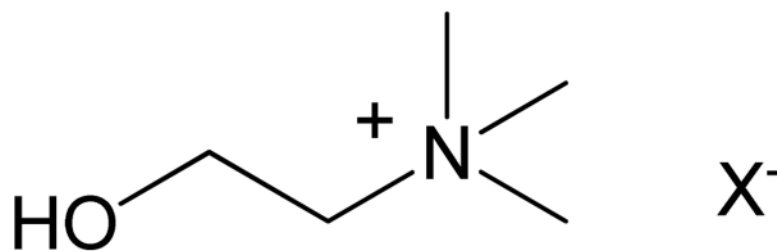|	IL	Temperature (°C)	Viscosity (mPa s)	Ref
1	[EMIM][Tf$_2$N]	20	34	[90]
2	[BMIM][Tf$_2$N]	20 25	52 49	[90] [91]
3	[HMIM][Tf$_2$N]	20	86	[92]
4	[OMIM][Tf$_2$N]	25	93	[93]
5	[EMIM][OAc]	20	162	[90]
6	[BMIM][OAc]	20 25	646 393	[92] [94]
7	[EMIM][BF$_4$]	20	45	[95]
8	[BMIM][BF$_4$]	25	105	[26]
9	[OMIM][BF$_4$]	20	135	[26]
10	[BMIM][PF$_6$]	20 25	308 207	[26] [96]
11	[OMIM][PF$_6$]	20	857	[26]
12	[OMIM]Cl	25	20,883	[97]
13	[CH$_3$O(CH$_2$)$_2$MIM][BF$_4$]	20	263	[26]
14	[CH$_3$O(CH$_2$)$_2$MIM][PF$_6$]	20	284	[26]
15	[CH$_3$(OCH$_2$CH$_2$)$_2$-MIM]Cl	20	613	[26]
16	[CH$_3$(OCH$_2$CH$_2$)$_2$-MIM][BF$_4$]	20	377	[26]
17	[CH$_3$(OCH$_2$CH$_2$)$_2$-MIM][PF$_6$]	20	426	[26]
18	[CH$_3$(OCH$_2$CH$_2$)$_2$-Et-Im][OAc]	20	92	[67]
19	[CH$_3$(OCH$_2$CH$_2$)$_3$-Et-Im][OAc]	20	92	[67]
20	[CH$_3$(OCH$_2$CH$_2$)$_2$-Et$_3$N][OAc]	20	132	[67]
21	[CH$_3$(OCH$_2$CH$_2$)$_3$-Et$_3$N][OAc]	20	147	[67]
22	[CH$_3$(OCH$_2$CH$_2$)$_3$-Et-Im][Tf$_2$N]	20	59	[98]
23	[CH$_3$(OCH$_2$CH$_2$)$_3$-Et$_3$N][Tf$_2$N]	20	63	[98]
24	[CH$_3$(OCH$_2$CH$_2$)$_3$-Me-Et-Im][Tf$_2$N]	20	85	[98]
25	[Bu-Et$_2$-MeN][Tf$_2$N]	25	120	[38]
26	[CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][Tf$_2$N]	25	69	[38]
27	[Bu-Et$_2$-MeN][CF$_3$BF$_3$]	25	210	[38]
28	[CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][CF$_3$BF$_3$]	25	108	[38]
29	[Bu-Et$_2$-MeN][C$_2$F$_5$BF$_3$]	25	104	[38]
30	[CH$_3$OCH$_2$CH$_2$-Et$_2$-MeN][C$_2$F$_5$BF$_3$]	25	68	[38]
31	[CH$_3$OCH$_2$CH$_2$-**MIM**][CF$_3$BF$_3$]	25	43	[35]
32	[CH$_3$OCH$_2$CH$_2$-**MIM**] [C$_2$F$_5$BF$_3$]	25	38	[35]

	IL	Temperature (°C)	Viscosity (mPa s)	Ref
33	[CH$_3$OCH$_2$CH$_2$-Me-**Pyr**] [C$_2$F$_5$BF$_3$]	25	52	43, 44
34	[CH$_3$OCH$_2$CH$_2$-Me-**PI**] [C$_2$F$_5$BF$_3$]	25	112	43
35	[CH$_3$OCH$_2$CH$_2$-Me-**OX**] [C$_2$F$_5$BF$_3$]	25	90	43
36	[CH$_3$OCH$_2$CH$_2$-Me-**MO**] [C$_2$F$_5$BF$_3$]	25	260	43
37	[CH$_3$OCH$_2$CH$_2$-**MIM**][Tf$_2$N]	20	54	90
38	[CH$_3$OCH$_2$CH$_2$-Et$_3$**P**] [Tf$_2$N]	25	44	40
39	[CH$_3$OCH$_2$CH$_2$-Et$_3$**N**] [Tf$_2$N]	25	85	40
40	[CH$_3$OCH$_2$CH$_2$-Me-**LG**] [Tf$_2$N]	25	58	45
41	[CH$_3$OCH$_2$CH$_2$-Me-**CG**] [Tf$_2$N]	25	46	45
42	[CH$_3$OCH$_2$CH$_2$-Me-**PI**] [Tf$_2$N]	25	55 102	39 43
43	[CH$_3$OCH$_2$CH$_2$-Me-**Pyr**] [Tf$_2$N]	25	53	43
44	[CH$_3$OCH$_2$CH$_2$-Me-**OX**] [Tf$_2$N]	25	117	43
45	[CH$_3$OCH$_2$CH$_2$-Me-**MO**] [Tf$_2$N]	25	310	43
46	[CH$_3$OCH$_2$CH$_2$-Et$_2$**S**] [FSI]	25	26	46
47	[BMIM][Me$_2$PO$_4$]	20	696	31
48	[MeOCH$_2$CH$_2$-MIM][Me$_2$PO$_4$]	20	769	31
49	[OMIM][Me$_2$PO$_4$]	20	1182	31
50	[Me(OCH$_2$CH$_2$)$_2$-MIM] [Me$_2$PO$_4$]	20	398	31
51	[Me(OCH$_2$CH$_2$)$_3$-MIM] [Me$_2$PO$_4$]	20	324	31
52	[HO(CH$_2$)$_2$MIM][BF$_4$]	20	91	26
53	[HO(CH$_2$)$_2$MIM][PF$_6$]	20	149	26
54	[HO(CH$_2$)$_2$MIM][Tf$_2$N]	25	91	91
55	[CH$_3$CH(OH)CH$_2$MIM][PF$_6$]	25	319	75
56	[CH$_3$CH(OH)CH$_2$MIM][Tf$_2$N]	25	342	75
57	[CH$_3$CH$_2$CH$_2$-Me-Pyr][Tf$_2$N]	25	54	91
58	[HOCH$_2$CH$_2$-Me-Pyr][Tf$_2$N]	25	80	91
59	[CH$_3$(CH$_2$)$_5$-Me-Pyr][Tf$_2$N]	25	96	91
60	[HOCH$_2$CH(OH)CH$_2$-Me-Pyr][Tf$_2$N]	25	1500	91
61	[CH$_3$CH$_2$CH$_2$-Me$_2$-^{i}Pr-N][Tf$_2$N]	25	113	91
62	[HOCH$_2$CH$_2$-Me$_2$-^{i}Pr-N][Tf$_2$N]	25	211	91
63	[HOCH$_2$CH$_2$-MIM][BF$_4$]	25	86	27
64	[H(OCH$_2$CH$_2$)$_2$-MIM][BF$_4$]	25	201	27
65	[H(OCH$_2$CH$_2$)$_3$-MIM][BF$_4$]	25	391	27
66	[HOCH$_2$CH$_2$-MIM][PF$_6$]	25	336	27
67	[H(OCH$_2$CH$_2$)$_2$-MIM][PF$_6$]	25	370	27
68	[H(OCH$_2$CH$_2$)$_3$-MIM][PF$_6$]	25	864	27

	IL	Temperature (°C)	Viscosity (mPa s)	Ref
69	[HOCH$_2$CH$_2$-MIM][Tf$_2$N]	25	541	[27]
70	[H(OCH$_2$CH$_2$)$_2$-MIM][Tf$_2$N]	25	922	[27]
71	[H(OCH$_2$CH$_2$)$_3$-MIM][Tf$_2$N]	25	2,249	[27]

Note the following abbreviations: pyrrolidinium (Pyr), methylimidazolium (MIM), oxazolidinium (OX), piperidinium (PI), morpholinium (MO), linear guanidinium (LG), cyclic guanidinium (CG), and bis(fluorosulfonyl)imide (FSI), 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-3-methylimidazolium (BMIM), 1-hexyl-3-methylimidazolium (HMIM), 1-octyl-3-methylimidazolium (OMIM).