IONIC LIQUIDS

1. Introduction

This article deals with the literature on ionic liquids, with the focus on nomenclature, preparation, and handling of the second-generation ionic liquids. In the older (and some current) literature, ionic liquids are sometimes called liquid organic salts, fused salts, molten salts, ionic melts, NAILs (nonaqueous ionic liquids), room-temperature ionic liquids, OILs (organic ionic liquids) and ionic fluids. Their most prominent feature, namely the potential of tuning their physical properties to suit a particular application, is discussed in detail. In addition, areas in which ionic liquids are already applied, and in which their properties promise favorable application in transition-metal catalyzed reactions, are reviewed.

In recent years, many ionic liquids have emerged as environmentally benign alternatives to volatile organic compounds (VOCs, such as trichloromethane, ethanenitrile and dimethylmethanamide), which cause emissions and effectively damage the ecological balance. The merit of ionic liquids, in this respect, is their negligibly small vapor pressure; therefore they are easily retained in a process (1). This concept has been realized, especially in preparative chemistry, as shown in many examples in this article: when used as solvents in catalytic processes, separation of the solvent (and the catalyst) from the product is facilitated, and recycling is easily possible.

2. Definition of Ionic Liquids

The term "ionic liquid" should be literally understood as a liquid that consists entirely of ions, as opposed to an ionic *solution*, which is a solution of a salt in a molecular solvent (Fig. 1). Similarly, eutectic mixtures of ionic liquids with molecular organic species are not ionic liquids, either.

However, there are tremendous differences in the physical behavior of ions in their molten state, depending on the nature of the ions. For example, molten salts derived from the compounds as shown in eqs. 1–3 (where $[\mathrm{pyH}]^+$ = pyridinium) may be thermally unstable, because they are in equilibrium with their conjugate base and acid, and the equilibrium constant is relatively high. The decomposition products (right hand side of the equilibrium) are responsible for the fact that these compounds possess a vapor pressure. From a review by Pagni (2), it becomes obvious that such labile melts are not inert and take part in a range of different reactions.

$$[\mathrm{pyH}]\mathrm{Cl} \rightleftharpoons \mathrm{py} + \mathrm{HCl} \tag{1}$$

$$[\mathrm{HNEt_3}]\mathrm{Cl} \rightleftharpoons \mathrm{NEt_3} + \mathrm{HCl} \tag{2}$$

$$\mathrm{Na}[\mathrm{Al_2Cl_7}] \rightleftharpoons \mathrm{NaCl} + \mathrm{Al_2Cl_6} \tag{3}$$

In stable molten salts, on the other hand, the equilibrium between reactants and the product lies far to the left hand side, resulting in immeasurably small vapor pressures. The patent literature appears to be concerned with

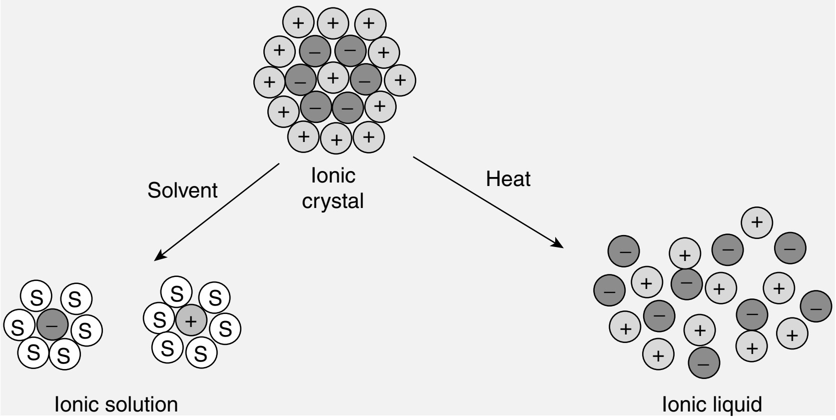


Fig. 1. Difference between an ionic solution and an ionic liquid.

distinguishing between high-temperature molten salts (melts) and room-temperature molten salts (ionic liquids). Although there is no specific reason to use any particular cut-off temperature, the current work may be seen in the context of green chemistry. From this perspective, process temperatures should be kept minimal, and ionic liquids have been defined (since 1914, Ref. 3) to be stable molten salts with melting point of around or below 100°C. However, this is completely arbitrary, and has no chemical rationale. Indeed, a good case can be made for completely removing the distinction, and regarding both categories as simply ionic liquids at a given temperature.

From a practical point of view, ionic liquids that fall within this working definition can be divided into three categories: first-generation; second-generation; and third-generation ionic liquids (4).

First-generation ionic liquids consist of bulky cations such as 1,3-dialkylimidazolium (or *N,N′*-dialkylimidazolium) or 1-alkylpyridinium (or *N*-alkylpyridinium), and anions based mostly on haloaluminate(III); these have been studied extensively. The merit of these ionic liquids is their tuneable Lewis acidity: the addition of aluminium(III) chloride to 1-ethyl-3-methylimidazolium chloride at a mole ratio of 1:1, for example, leads to the formation of Lewis neutral $[AlCl_4]^-$. Larger amounts of added aluminium(III) chloride bring about the formation of anions such as $[Al_2Cl_7]^-$ (5) and $[Al_3Cl_{10}]^-$ (6), which are both Lewis and Franklin acids.

The drawback of these systems is their great sensitivity towards water, which forms hydroxoaluminate(III) species with the aluminium(III) chloride and therefore decomposes the ionic liquid (7). The sensitivity towards water necessitates their handling in a dry-box. Nevertheless, typical chemistry promoted by Lewis acids was carried out in these ionic liquids, such as Friedel-Crafts reactions (8–11), alkylation of alkanes with alkenes (12,13), nickel-catalyzed dimerization of ethene (14,15), propene (16) and butene (17,18), olefin metathesis (19), butene oligomerization (14,20), Ziegler-Natta-type ethene polymerization (21), poly(phenylene) synthesis by oxidative dehydropolycondensation of benzene (22), poly(ethene) cracking (23), selective hydrogenation of aromatic compounds (24) and Diels-Alder reactions of cyclopentadiene with either methyl acrylate or dimethyl maleate (25). These reactions have been carried out in Lewis acidic (or, more correctly, Franklin acidic (26) ionic liquids), and are well reviewed in the literature (4,27–30), and hence they are not considered any further in this discussion. Also, research related to polymers which structurally resemble ionic liquids, ionic gels and zwitterions is not covered here, but the interested reader is referred to an excellent book edited by Ohno (31).

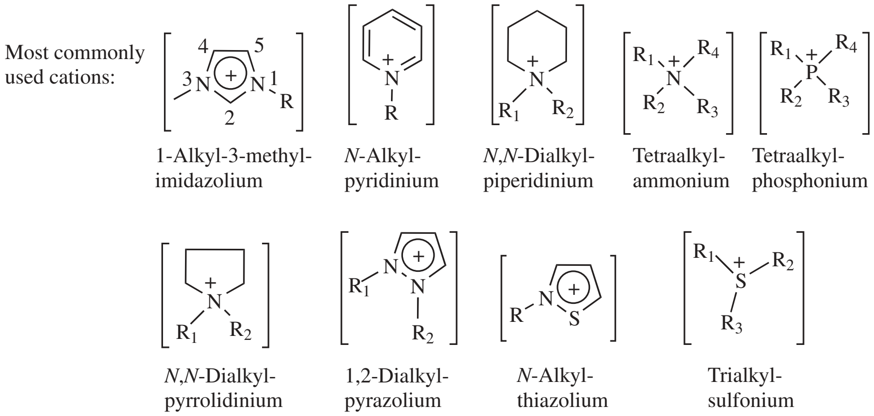
The ionic liquids of the second category, the so-called second-generation ionic liquids, are discussed in detail in this article: they are usually air-stable and water-stable (see Section 7.2), and can be used on the bench-top. However, as discussed in detail in Section 8.9, it should be noted that water-stable does not imply that there is no interaction with water – all second-generation ionic liquids gradually absorb water from the atmosphere (32).

Recently, a third generation of "task-specific" ionic liquids has emerged: these novel ionic liquids feature chemical functionalities which have been designed for specific applications. Very little is known to date about their physical properties, preparative methods, etc, and the future will show if they can bring about an ecological or economic benefit; but that future does look bright!

3. History and New Developments

The earliest reported salts, which would nowadays qualify as ionic liquids, are the alkylammonium nitrates ($[NR_4]^+$, $[NR_3H]^+$, $[NR_2H_2]^+$, $[NRH_3]^+$, where R = Me, Et, or Pr). These were investigated by Paul von Walden in 1914, specifically because of their low melting points, a prerequisite for his conductivity measurements (3). In 1934, Graenacher used 1-benzylpyridinium chloride to aid dissolution of cellulose (33). Historically (34), ionic liquids have been developed from the traditional high-temperature molten salts (like eutectics from LiCl and KCl), and the somewhat lower melting inorganic chloroaluminate(III) systems (eg, NaCl-Al_2Cl_6 eutectics), which were studied as electrolytes for thermal batteries (27,35). Reference 34 gives a first-hand account of the historical background of the subject. In the quest of finding lower melting salts, Hurley and Wier investigated ionic liquids based on 1-ethylpyridinium bromide and aluminium(III) chloride (36). Almost a generation later, the groups around Osteryoung and Hussey reported the first genuine room-temperature ionic liquid based on 1-butylpyridinium chloride and aluminium(III) chloride (8,37), which has exceptionally low lattice energies. However, for battery applications, which were their main interest, the pyridinium salts were too easily reduced. In 1982, Wilkes and co-workers developed 1,3-dialkylimidazolium chloroaluminate(III) salts, which possess a larger HOMO-LUMO gap (5), and are also liquid at room-temperature. Indeed, some compositions were liquid at temperatures as low as -96°C. A few years later, water-stable anions such as tetrafluoroborate (but see Section 7.2), nitrate and ethanoate, were investigated to replace the chloroaluminate(III) anions (38). Although initially intended to be candidates for battery electrolytes, these ionic liquids have shown to be useful in many other applications (34).

Seddon and co-workers (39) and Wilkes and Zaworotko (38) proved the concept that the systematic alteration of the cation and the anion, respectively, can



$R_{1,2,3,4} = CH_3(CH_2)_n$, ($n$ = 0, 1, 3, 5, 7, 9); aryl; *etc.*

Some possible anions:

Water-immiscible	⟶	Water-miscible
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[NTf_2]^-$	$[OTf]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$	$[N(CN)_2]^-$	Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Fig. 2. Some commonly used ionic liquid systems.

be used to “fine-tune” the properties of an ionic liquid. Typical cations and anions, which have been combined to yield ionic liquids, are shown in Fig. 2.

This work was predated in the literature by earlier studies of ammonium and phosphonium salts (40–43). In fact, Parshall obtained similar results in low melting tetraethylammonium or methyltriphenylphosphonium salts for platinum-catalyzed hydrogenations, carbonylation, hydroformylation, and isomerization reactions as in organic solvents. He realized the potential of these novel solvents in biphasic catalysis, allowing for easy phase separation and catalyst recycling (40). Indeed, the following quote reveals amazing prescience (40):

> *A major problem in homogeneous catalysis is the separation of products from the catalyst* ... An approach that seems under utilised is the use of molten salts as stable, non-volatile solvents from which organic products are readily separated by distillation ... A substantial advantage of the molten salt medium, however, is that the product may be separated by decantation or simple distillation.

Tetraalkylammonium derivatives (44,45) were reported to be thermally unstable, but they are mentioned here, due to their historical significance and their relevance as phase-transfer catalysts (46).

Besides the principally investigated 1-alkyl-3-methylimidazolium and 1-alkylpyridinium cations, other more recent developments include cations such as trialkylsulfonium (47,48), alkyl-substituted thiazolium salts (49–52), 1-alkyl-1-methylpyrrolidinium (53–56), 1,2-dialkylpyrazolium (57,58), dialkylmorpholinium (56), guanidinium (59), 2-alkyl-isoquinolinium (60), cations derived from the antifungal drug miconazole (61) or from the "chiral pool" (62–64). Also, various ammonium cations have been prepared bearing side-chain functionalities ("task-specific ionic liquids") such as alkene- (65), alkyne- (66), ester-, hydroxyl- or chloro- (67,68), fluoro- (69,70), ether- (68,71), sulfonate- (71), carbonyl- (72), nitrile- (66), thiourea-, thioether- and urea-substituents (51,73). These new, third-generation ionic liquids are often referred to as task-specific ionic liquids.

Figure 2 also shows some of the commonly used anions. Other anions have also been used, including tricyanomethanide (74), $[Co(CO)_4]^-$ (75), isocyanates and cyanates (51), $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$ (76), $[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, $[IrCl_6]^{2-}$ (77), $[PdCl_4]^{2-}$ (78), $[AuX_4]^-$ (52,79), $[NbF_6]^-$, $[TaF_6]^-$ (80), and chiral anions, such as lactate and tartrate (81).

3.1. Ionic Liquids as Designer Solvents.

The above summary is not meant to be comprehensive, but it highlights the versatility and tunability of ionic liquids: depending on the application, the ionic liquid is designed for performance (*designer solvents*) (82). In fact, it has been predicted that at least one million simple ionic liquids and at least one trillion (10^{18}) ternary ionic liquids can be prepared from the combination of anions, cations, and substituents (83). In addition to all these diverse cations, mixtures of several anions and cations may be used as well (84). In fact, over 30,000 entries for 1,3-functionalized imidazolium derivatives are recorded in the CAS database.

Both advantages and pitfalls lie in this enormous choice: although there is certainly an optimal ionic liquid for any given application, it requires a lot of experience to find the needle in the haystack. The choice of the anion and cation not only influences the physical properties, but also, if used as solvent, the thermodynamics and the kinetics of a reaction. Thus, by optimizing the solvent, the reaction outcome can be improved and controlled. At a zeroth level approximation, the anion controls the chemistry, and the cation fine-tunes the physical properties such as solubility, density, viscosity, etc. As an example, the nature of the anion may determine if the ionic liquid will be water-miscible (eg, I^-) or not (eg, $[NTf_2]^-$) (*vide infra*). Thus tuning the properties of the solvent to suit a particular application is feasible (85).

4. Nomenclature

This discussion includes ionic liquids derived from the 1-alkyl-3-methylimidazolium and the 1-alkylpyridinium cation; the former is abbreviated $[C_n\text{mim}]^+$, where the index n accounts for the number of carbons in one of the linear alkyl chains, and mim stands for *N*-methylimidazolium. The 1-ethyl and 1-butyl derivatives are often referred to as $[\text{emim}]^+$ and $[\text{bmim}]^+$, for 1-*e*thyl-3-*m*ethyl*im*idazolium and 1-*b*utyl-3-*m*ethyl*im*idazolium, respectively. Some research groups continue this series of trivial names with $[\text{pmim}]^+$, $[\text{hmim}]^+$ and $[\text{omim}]^+$ for 1-pentyl-, 1-hexyl-, and 1-octyl-3-methylimidazolium, respectively. Since these abbreviations are not unambiguous, they should not be used, and $[\text{Hmim}]^+$ is reserved to represent the protonated 1-*H*-3-methylimidazolium cation. C-2-methylation (for numbering, see Fig. 2) of the imidazolium moiety leads to even more possibilities of different cation types. These cations are abbreviated $[C_n\mathrm{dmim}]^+$, for 1-alkyl-2,3-*dim*ethyl*im*idazolium, and $[C_n\mathrm{py}]^+$ stands for the 1-alkylpyridinium cation. For the quaternary phosphonium cations $[PC_wC_xC_yC_z]^+$ or $[P_{wxyz}]^+$ are normally used, where w, x, y and z indicate the length of the corresponding linear alkyl chains. Moieties commonly used, such as methyl, ethyl, butyl, phenyl etc, are sometimes abbreviated Me, Et, Bu, Ph. The nomenclature for quaternary ammonium cations follows the same principles.

Because in first-generation ionic liquids, such as the chloroaluminates, equilibria between various anionic species exist, their composition must be indicated. For example, a Lewis acidic ionic liquid prepared from $[C_n\mathrm{mim}]\mathrm{Cl}$ and $\mathrm{AlCl_3}$ in a mole ratio of 1:2 does not contain free aluminium(III) chloride, but chloride, $[\mathrm{AlCl_4}]^-$, $[\mathrm{Al_2Cl_7}]^-$, and higher oligomers. In order to symbolize this, it is abbreviated $[C_n\mathrm{mim}]\mathrm{Cl}\text{-}\mathrm{AlCl_3}$ ($X = 0.67$), where X equals the mole fraction of nominal $\mathrm{AlCl_3}$. The anions of the second-generation ionic liquids are given by their commonly used formulae, and trifluoromethylsulfonate (or triflate) and bis{(trifluoromethyl)sulfonyl}amide (or bistriflamide, often incorrectly, referred to as an imide rather than an amide) are abbreviated $[\mathrm{OTf}]^-$ and $[\mathrm{NTf_2}]^-$, respectively. The various systems are usually classified by anions, eg, nitrate, tetrafluoroborate, etc. According to IUPAC nomenclature, a square bracket is drawn around polyatomic ions, and monoatomic anions are denoted without brackets. Thus $[C_4\mathrm{mim}]\mathrm{Cl}$ is correct, $[C_4\mathrm{mim}][\mathrm{Cl}]$ is not; $[C_4\mathrm{mim}][\mathrm{NTf_2}]$ is correct, $[C_4\mathrm{mim}]\mathrm{NTf_2}$ is not; the cation (if organic) must always be enclosed by square brackets.

5. Laboratory Synthesis

In the laboratory, the common first step of the synthesis of both first- and second-generation ionic liquids is identical. Thus, imidazolium-based ionic liquids are derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide (which is an ionic liquid itself, if the melting point is lower than 100°C), in most cases the chloride. This precursor is prepared by the alkylation of 1-methylimidazole in a Menschutkin-type reaction (86), as depicted in Fig. 3. If the chloroalkane is gaseous at room temperature, eg, chloroethane, the alkylation is usually carried out in an autoclave, at autogenous pressures and 90°C, without addition of solvent. Higher homologues can be prepared under reflux at atmospheric pressure. The preparation of the 1-alkylpyridinium (87) or 1-alkyl-2,3-dimethylimidazolium (88) derivatives follows the same method, starting from pyridine or 1,2-dimethylimidazole, respectively.

This intermediate salt is then either used in a metathetic reaction (ion exchange), where the 1-alkyl-3-methylimidazolium halide (in most cases the chloride) is exchanged with the anion of a Group 1 metal or silver(I) salt, MY. Otherwise, it is treated with an acid, HY (see Fig. 3). These reactions are stoicheiometric, and therefore equimolar amounts of waste MX or HX are produced. Both methods are carried out in water at room-temperature, although some authors use organic solvents (70). Depending on the anion (and, to a lesser extent, the cation) chosen, the resulting ionic liquid forms either a biphasic system with water, or a homogeneous solution. In the former case (eg, if the anion is

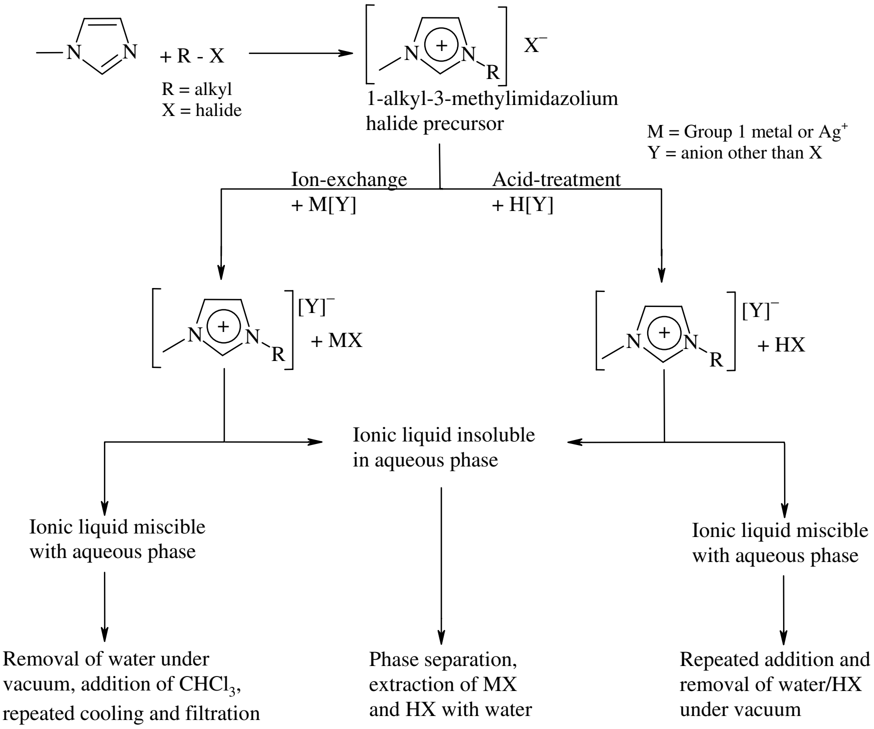


Fig. 3. Common routes for the preparation of ionic liquids.

$[PF_6]^-$ or $[NTf_2]^-$), an aqueous extraction follows to remove the excess of chloride (MX or HX, or any unreacted starting material). For water-miscible ionic liquids, the work-up of the metathetic reaction involves the removal of water under reduced pressure, addition of trichloromethane, and repeated cooling to 5°C to precipitate MX (89), followed by several filtration steps. The work-up of the water-miscible ionic liquids prepared by treatment with acid includes repetitive addition of water and removal of water/HX under reduced pressure and elevated temperature. In both cases, this is very cumbersome and the effectiveness of the removal of chloride is only mediocre (32). Halide-free ionic liquids can be obtained in the metathetic reaction, if a silver(I) salt is used instead of a Group 1 metal salt, and residual silver ions can be removed quantitatively by electrolysis (90). However, this method is expensive and involves yet another clean-up stage, and silver salts are produced as by-products. A procedure involving lead(II) salts (91) has been shown not to be viable (92). Due to the fact that water-immiscible ionic liquids are easier to prepare than water-miscible ones, these are much more investigated in the literature at present.

Recently, the ion-exchange resin Amberlyst A27 was employed to make $[C_4mim]_2[SO_4]$ from $[C_4mim]Cl$. $[C_4mim]_2[SO_4]$ was then used as starting material for the hydrogensulfate analogue by addition of a stoicheiometric amount of sulfuric acid. An anion exchange in an aqueous phase between two salts

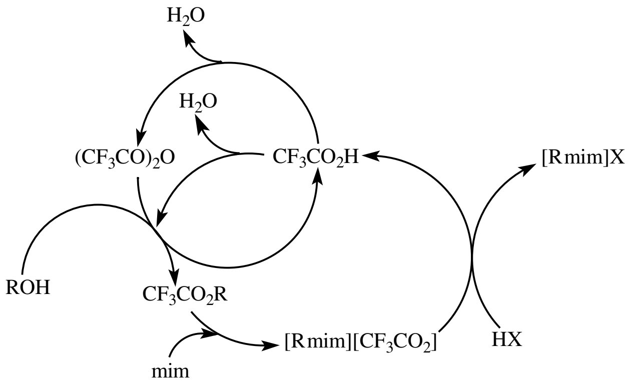


Fig. 4. Preparation of a halide-free ionic liquid with trifluoroethanoic acid (64).

([NBu_4][HSO_4] and [C_8mim][NTf_2]) can be used to produce [C_8mim][HSO_4] by extraction with dichloromethane (93).

The production of equimolar amounts of waste can be circumvented by the direct alkylation of 1-methylimidazole with, for example, diethyl sulfate, alkyl trifluoromethylsulfonate or alkyl bis{(trifluoromethyl)sulfonyl}amide (70,94). Using this concept, Seddon and co-workers (64) invented a benign and halide-free method by first producing ionic liquids based on trifluoroethanoate from alkyl trifluoroethanoate, and subsequent exchange of the trifluoroethanoate with an acid HX. The trifluoroethanoic acid formed has a low boiling point of 72°C, and can thus be easily separated by distillation, and directly recycled *via* esterification with the corresponding alcohol or by dehydration to the anhydride (Fig. 4) (64).

Alternatively, many amines (43), such as 1-methylimidazole, give protonated ionic liquids upon neutralization with an acid. Surprisingly, preliminary studies indicate that low melting salts with sufficient stability for electrochemical studies can be obtained thus (65,95,96).

Ionic liquids can also be prepared from their corresponding carbenes; to achieve this, the chloride precursor is heated in a Kugelrohr apparatus (97) in the presence of a base, such as potassium *t*-butoxide (see Fig. 5), yielding potassium chloride, *t*-butanol and the carbene, which is isolated by distillation. This method of preparation is not applicable to ionic liquids other than 1,3-dialkyl-imidazolium-based salts (64).

The addition of a carbene (eg, 1-butyl-3-methylimidazol-2-ylidene in Fig. 6) to acids yields clean, chloride free-ionic liquids (64,98).

In an attempt to tackle the expeditious preparation of ionic liquids, and to allow for effective industrial use, a mixture of 1,3-dimethyl-, 1-butyl-3-methyl- and 1,3-dibutyl-imidazolium tetrafluoroborates were prepared in a one-pot reaction of formaldehyde, butylamine, methylamine, H[BF_4], and glyoxal, thus circumventing the introduction of halide impurities and tedious separations. This mixture was used as solvent in the hydrogenation of poly(acrylonitrile-butadiene) to afford speciality polymers using [RuHCl(CO)(PCy_3)$_2$] as catalyst precursor (99).

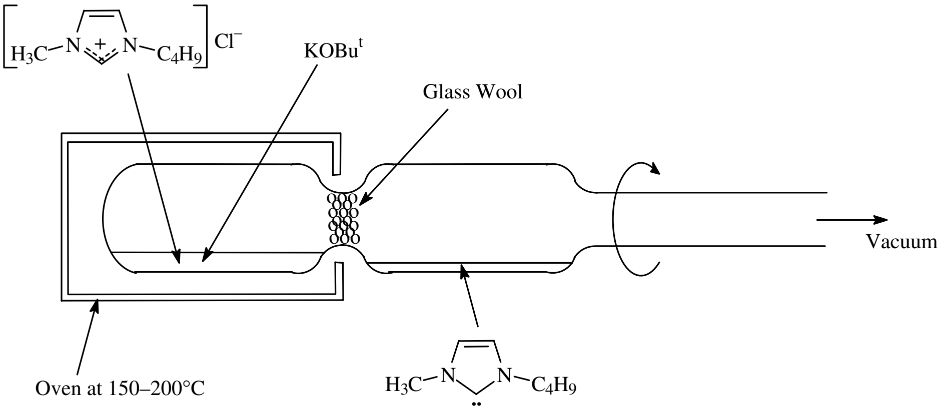


Fig. 5. Kugelrohr apparatus for the preparation of a typical carbene (64,98).

The use of microwave reactors (100,101) for the alkylation step has been studied by various authors. It was found that reaction rates were increased by factors of 70 to 110 on a 110 mmol scale with only 1.1 equivalents excess of the haloalkane compared to conductive heating. On a larger scale (up to 2 mol) (101), a reflux apparatus may be used within the reactor cavity, leading to 200–400 times shorter reaction times in a solventless system than literature reports.

Ionic liquids based on phosphonium cations are prepared in a similar fashion to the imidazolium (and other ammonium) ionic liquids: a trialkylphosphine is alkylated either using a chloroalkane, phenyl alkyl sulfonate, or similar esters (102). The trisubstituted precursor may be derived from the reaction of phosphine with a single alkene, or a mixture of two alkenes, resulting in a symmetrical (PR_3) or unsymmetrical (PRR'_2) trialkylphosphine, respectively (102).

Although theoretically colorless, ionic liquids often have a yellow to brown tint (or, in extreme cases, black!), the origin of which is still unknown. Although the nature of the impurity can not be determined spectroscopically, and has no apparent influence on reaction outcomes or physico-chemical properties, some methods were developed for its removal using decolorizing carbon and neutral alumina (103–106). The impurity is believed to be intensely colored, and only present at parts per billion levels.

A large number of ionic liquids are now commercially available in gram to multi-ton scale from, *inter alia*, Merck KGaA/EMD Chemicals Inc., Cytec, DuPont, SACHEM, BASF Solvent Innovation, and Acros (107).

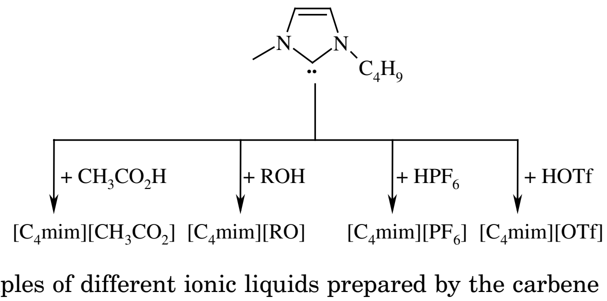


Fig. 6. Examples of different ionic liquids prepared by the carbene method (64,98).

6. Determination of Impurities

Very little attention has been paid to analytic issues regarding the purity of ionic liquids. This is mainly due to the fact that their negligibly low vapor pressure excludes analysis by gas-phase based methods, eg, gas chromatography. Another convenient indicator for purity, the melting point of a compound, is also not viable, because ionic liquids are often liquids at room-temperature, and often form glasses on freezing, rather than crystals.

In general, impurities stem from the preparation of the ionic liquid (water, halide, and amine) (108,109) or from the absorption of water from the atmosphere (32,70,85). Critically, they have a strong influence on the physicochemical properties (32,110). For example, the reported melting point for the *same* ionic liquid varies considerably, ie, for $[C_2mim][BF_4]$: 15°C (38), 5.8°C (4), 12.0 to 12.5°C (111), 11°C (112) and 14.6°C (113). Additionally, it was reported that halide anions may contribute to corrosion of the reactor walls (114), deactivate transition metal catalysts, and lead to a reduced rate of reaction or selectivity (18,19,99,115–127). An extensive study of the effects of impurities such as chloride, 1-methylimidazole or water on the metathesis of oct-1-ene using Grubbs' first generation catalyst precursor showed that already very low levels of these impurities may suppress the reaction considerably (128).

Several authors have described the quantitative determination of halide impurities by Volhard titration (32), ion selective electrode (32), electrophoresis (129), ion chromatography (130) or electrochemical techniques (131), thus allowing for the detection of impurities on ppb level. The water content can be determined very conveniently by automated Karl-Fischer titration (70), and residual amine content can be established either by a spectroscopic (132) or chromatographic method (128).

Reported literature data are only worthwhile if the results are accompanied by the relevant analytical specifications; this means that, at present, much published "data" have little or no value.

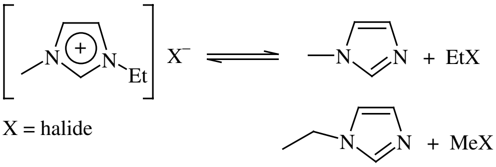
7. Stability

7.1. Thermal Stability.

Except for the physical properties, the thermal and chemical stability of an ionic liquid will determine its applicability in a reaction. At present, little is known about the instability of ionic liquids, although from an industrial application point of view, this aspect might be one of the most important factors.

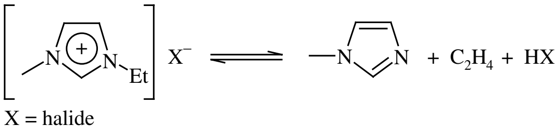
Many researchers have observed that ionic liquids often alter in their color, depending on the method of preparation. For instance, when heated above 80°C at reduced pressure to remove traces of water, ionic liquids frequently turn dark-brown, whereas they stay almost colorless when heated gently. Gale and Osteryoung (133) attributed this observation to the formation of impurities by degradative side-reactions (134). The nature of these colored impurities is yet unknown, and they are not detectable by NMR or other spectroscopic methods (135). However, recent investigations under high thermal stress (sonication at 135°C) reported that the thermal decomposition products of 1-butyl-3-methylimidazolium chloride include chlorobutane, chloromethane, and imidazole decomposition products such as buta-1,3-diene, butadi-1,3-yne, ethanenitrile/isocyanomethane, 2-methylpropane, 2-propenenitrile and pent-3-en-1-yne (135).

These results are apparently supported by earlier reports, which stated that imidazolium-based ionic liquids decompose by a similar mechanism (136) to that found for tetraalkylammonium (43,45) and 1-alkylpyridinium salts (134) *via* two pathways. The reversed Menschutkin reaction (86) is the back-reaction of the preparation, where the halide attacks the alkyl group *via* an S_N2 mechanism, leading to dealkylation as shown in eq. 4. Other anions, such as thiosulfate, thiocyanate, sulfide, hydrogensulfite and bis(methylsulfonyl)-amide have been reported to support this reaction due to their weakly basic and polarisable properties (43).



(4)

A secondary decomposition reaction also occurs, *via* the Hofmann degradation, in which an alkene is formed. For $[C_2mim]Cl$, it results in the formation of ethene and hydrogen chloride (136), and the reaction is shown in eq. 5.



(5)

The Hofmann reaction is dependent on the nucleophilicity of the anion X^-. In tetraalkylammonium salts (45), the rate of alkene formation increases in the order:

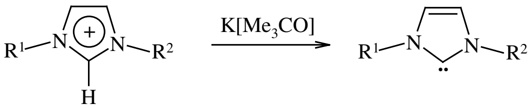
$$[NO_3]^- < [SCN]^- < I^- < Br^-$$

Alkene formation is not observed in ionic liquids containing relatively non-nucleophilic anions such as $[BF_4]^-$, $[OTf]^-$, $[NTf_2]^-$, or $[PF_6]^-$ (45). The reaction was shown to be dependent on the extent of the reversed Menschutkin reaction; the olefin is formed by a dehydrohalogenation of RX by R_3N, a known side-reaction in the Menschutkin reaction (45).

Early, and unfortunately current, investigations overestimate the thermal stability (placing them at 400°C and higher) of many 1,3-dialkylimidazolium-based ionic liquids by thermogravimetric analysis (70,110,137,138). Since the heat transfer in ionic liquids is slow, the sample temperature lags behind the measured temperature by between 75 and 150°C, at the high heating rates (between 10 and 20°C min^{-1}) that were used. Under these conditions, the decomposition reaction does not reach equilibrium before the end of the experiment. The most accurate data require isothermal studies.

Under isothermal conditions, however, [C_4mim][OTf] shows long-term stability at 200°C (139), and for [C_2mim][NTf_2] a weight-loss of 1% was found over 10 h at 250°C (140).

7.2. Chemical Stability. 1-Alkyl-3-methylimidazolium-based ionic liquids possess acidic ring-protons at the C-2 position (see Fig. 2) which may be removed by bases (eg, potassium *t*-butoxide, as shown in eq. 6) to give very stable carbenes (98). These carbenes are often referred to as Arduengo carbenes (141). Weaker bases, such as ethanoate, have the same effect (92); this reaction, however, proceeds more slowly, and does not go to completion (142). Nevertheless, if used as solvents in reactions with strong nucleophiles, the involvement of carbenes is always conceivable, eg, as ligands on transition metal catalysts. For example, the formation of the Heck catalyst precursor dibromobis(1-butyl-3-methylimidazol-2-ylidene)-palladium(II) from palladium(II) ethanoate in [C_4mim]Br in the presence of small amounts of sodium ethanoate, has been observed (143). Thus, both the anion and the cation of the ionic liquid play an important role in the formation of potentially catalytically active species.



(6)

Another example of carbene formation is the benzoin condensation, where a carbene intermediate, formed from the ionic liquid solvent, acts as catalyst (50).

In base-catalyzed reactions, the participation of the 1-alkyl-3-methylimidazol-2-ylidene in the catalytic cycle can be prevented by "blocking" the C-2 position of the 1-alkyl-3-methylimidazolium cation by methylation to the 1-alkyl-2,3-dimethylimidazolium cation, or by changing to another inert cation, such as pyridinium.

Second-generation ionic liquids are mostly stable towards water and most organic chemicals. Exceptions are ionic liquids based on the hexafluorophosphate, $[PF_6]^-$, or tetrafluoroborate, $[BF_4]^-$, anions. When originally reported, these were believed to have been water stable (for no obvious reason, as inorganic chemists had long realized their hydrolytic instability). Equations 7 and 8 represent the complete hydrolysis of these anions, but there are many partially hydrolyzed species formed too:

$$[PF_6]^- + 4\,H_2O \rightarrow 2H^+ + 6\,HF + [PO_4]^{3-} \tag{7}$$

$$[BF_4]^- + 3\,H_2O \rightarrow 2H^+ + 4\,HF + [BO_3]^- \tag{8}$$

The first reported observation that hexafluorophosphate-based ionic liquids liberate hydrogen fluoride (eq. 7) in the presence of 10 *M* HNO_3 was from Rogers and co-workers (144); at high temperatures, the instability was much more marked. Hydrolysis also occurs with the tetrafluoroborate anion (145). Surprisingly to some, the tetrafluoroborate salts are even more readily hydrolysed than their analogous hexafluorophosphate salts. It is strongly recommended that ionic liquids based on these anions are never used in synthesis, unless the conditions are carefully controlled and monitored. A substantial number of papers are published every year in which syntheses carried out in these ionic liquids are reported, often with such terms as “autocatalytic” being used. These publications are totally worthless. The “autocatalytic” effect is conventional HF catalysis. Apart from the bad science generated, HF is extremely toxic and corrosive, and etches glass.

8. Characteristics

Because of the many variations possible for both the anion and the cation, and due to their differences in shape and size, an immense array of different ionic liquids is imaginable (see Section 3). In this way, ionic liquids constitute the largest group of solvents available. The properties of the solvent can be specifically designed by the deliberate combination of anion and cation. Thus, the physical properties such as melting point, viscosity and density can be tuned, and secondary properties, like solubility and reactivity of a specific substrate, are influenced as well. Ionic liquids possess therefore the potential to substitute for any molecular solvent, especially the banned halocarbons (146).

In the following sections, the physico-chemical behavior of second-generation ionic liquids is discussed; as mentioned earlier, this discussion does not include the strongly hygroscopic and water-sensitive first-generation ionic liquids, which are dealt with in detail elsewhere (4,27–30).

8.1. Phase Behavior and Liquid Range. The phase behavior of a compound describes its response to changes in temperature, pressure and concentration. In general, the melting point, which is a thermodynamic property, is defined as the temperature at which the solid and the liquid states of a compound are in equilibrium, and the freezing point equals the melting point (147). For some compounds, however, such as salts containing bulky cations and/or anions, the rate of attainment of the equilibrium between the liquid and solid state is kinetically restrained, eg, by the freezing or thawing of Brownian motion of longer chain segments, and thermodynamic equilibrium is not attained. If the viscosity of such compounds increases too quickly upon cooling, the molecules cannot achieve the optimal position necessary for crystallisation, and supercool into a glass (148). This phenomenon is also known as frustration of crystallization, and can lead to the phenomenon of polymorphism in many ionic liquids (see Section 10.1).

By definition, ionic liquids are salts that are liquid $<100^\circ$C. The formation of a closely packed lattice structure is avoided if the salt is composed of bulky and unsymmetrical cations or anions (149). For example, 1-alkylpyridinium derivatives melt at considerably higher temperatures than the imidazolium derivatives (28), due to the fact that the 1-alkylpyridinium cation possesses two mirror planes and a C_2 rotation axis that are not present in the 1-alkyl-3-methylimidazolium cation. Thus, the melting point of $[C_4py][BF_4]$ is 15.3°C (113), whereas the analogous $[C_4mim][BF_4]$ melts at -71°C (glass transition) (85).

It is therefore not surprising that many ionic liquids super-cool. In fact, all salts belonging to the $[C_n mim][BF_4]$ series ($n = 2-18$) have a tendency to supercool before crystallising ($n = 10-18$) or forming glasses ($n = 2-9$) (Fig. 7). Small variations in the length of the alkyl chain attached to the imidazolium moiety

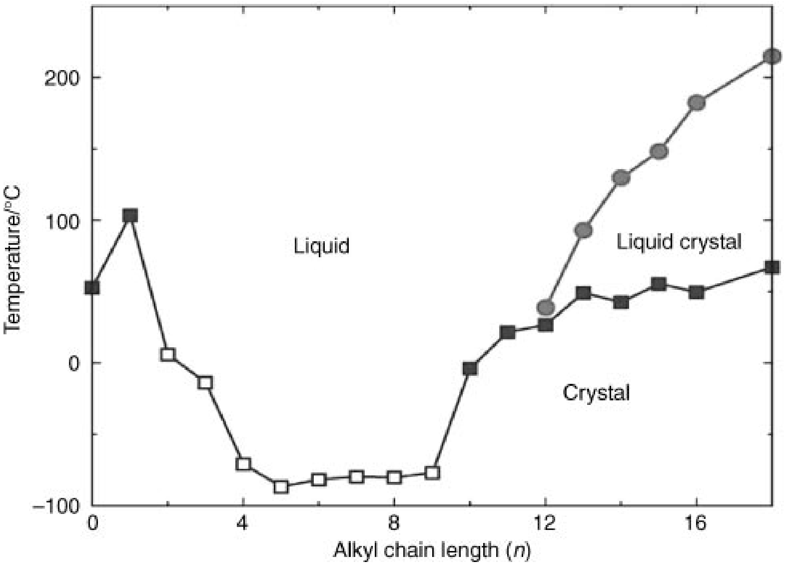


Fig. 7. Phase diagram of [$C_n$mim][BF_4]. Melting points (■), glass (☐) transitions and clearing points (●) (85).

lead to huge differences in the melting/freezing/glass-transition points. Interestingly, the glass-transition points for the salts with $n = 4–9$ are almost constant (variations between −70 to −90°C), but a huge increase is observed between $n =$ 9 and 10. The trend of rising transition temperatures as n increases beyond 8 is independent of the anion, and can be attributed to increased van der Waals forces between the alkyl chains, which override the effect of lower symmetry.

Another phenomenon is observed for salts of cations with long alkyl chains: the crystal structures of [C_{12}mim][PF_6], for example, and higher analogues are highly ordered and consist of layers with inter-digitated alkyl-chains (Fig. 8).

Upon heating, these higher analogues exhibit liquid crystalline phases over a specific temperature range. Liquid crystals are obtained when a crystal, upon heating, starts to become liquid, but maintains areas of order. Upon further heating, these ordered phases are disrupted as well, and a true isotropic liquid phase is obtained (85). The thermal range of the liquid crystalline phase markedly increases with increasing chain length. A similar phase behavior is found for both 1-alkyl-3-methylimidazolium-based ionic liquids (chlorides (151), tetrachlorometallates(II) (151), hexafluorophosphates (150)), and 1-alkylpyridinium hexafluorophosphates (150).

Various ionic liquids were investigated with respect to finding a direct relationship between the extent of hydrogen-bonding and their melting point. However, ionic liquids which exhibit a higher degree of hydrogen-bonding (eg, [C_2mim][O_2CCH_3]) show similar (low) glass-transition temperatures to those which are less prone to hydrogen-bonding (eg, [C_2mim][NTf_2]). Also, methylation in the C-2 position leads to an increase in melting point and formation of crystalline solids, rather than suppressing hydrogen-bonding and thus reducing the melting point (70,149). The authors concluded that the methylation aids

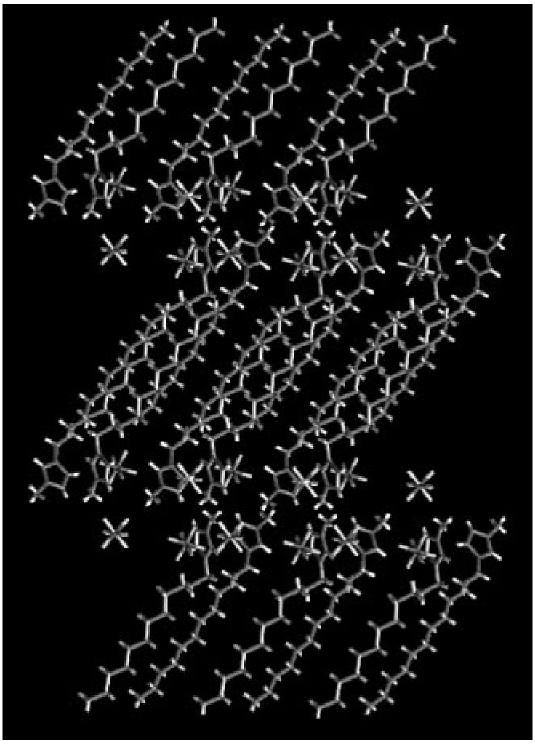


Fig. 8. Overall crystal structure for [C_{12}mim][PF_6] showing the inter-digitation and tilted alkyl chains (150).

packing efficiency by masking the asymmetry of the 1,3-dialkylimidazolium cation. This highlights the complexity of attempts to predict melting points, a particularly difficult task when the existence of polymorphs is also considered.

A particularly surprising phenomenon was reported in 2006 (152): not all ionic liquids are mutually miscible. When a hydrophobic ionic liquid is mixed with a hydrophilic ionic liquid, they may form mutually immiscible phases, some of which are also immiscible with solvents as diverse as water and alkanes (see Fig. 9); an archetypal biphasic system is trihexyltetradecylphosphonium chloride with 1-alkyl-3-methylimidazolium chloride (where the alkyl group is shorter than hexyl).

In summary, due to their complex phase behavior and high decomposition temperatures, ionic liquids often feature an exceptionally large liquid range. For example, the melting point of [C_4mim][OTf] is 16°C (70), with long-term stability at 200°C (139), and [C_2mim][NTf_2] melts at -3°C (70) and slowly decomposes at temperatures >250°C (140). This large range appears to be a generic feature of ionic liquids (*caveat emptor*: there are few accurate decomposition temperatures recorded in the literature), and contrasts to the standard pressure liquid ranges of water (100°C), dimethyl sulfoxide (170°C), liquid ammonia (45°C), or ethanoic acid (100°C).

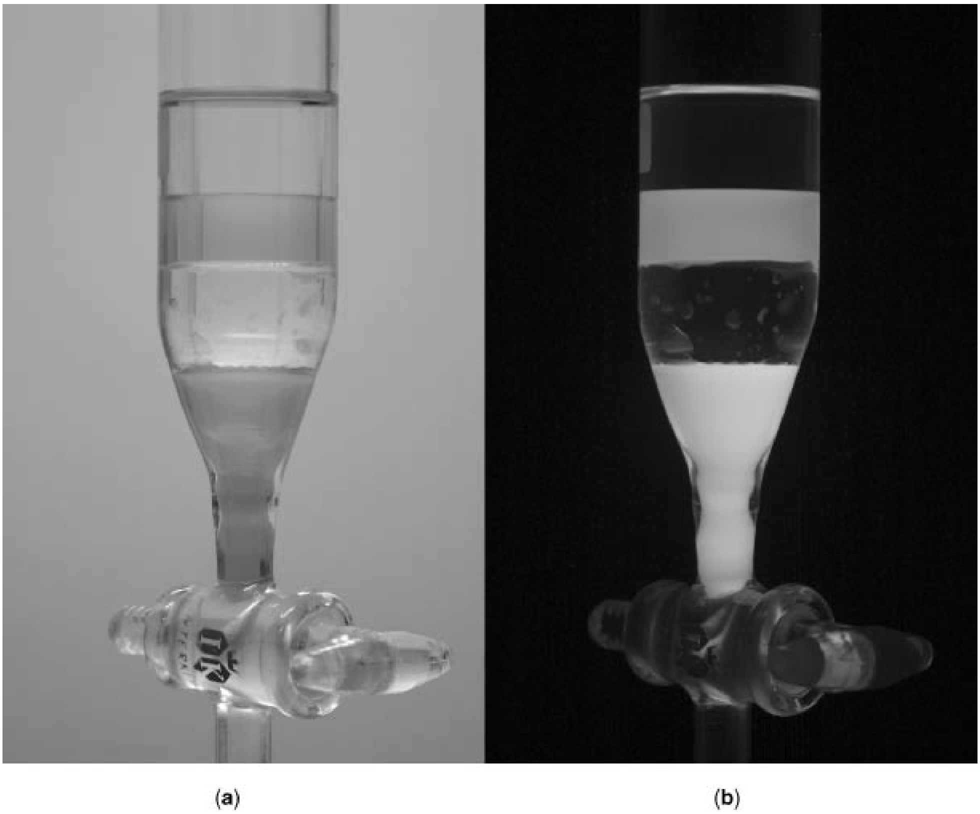


Fig. 9. A stable tetraphasic mixture of (from top to bottom): pentane, $[P_{6\,6\,6\,14}][NTf_2]$, water and $[C_2mim][NTf_2]$. The pink dark in (**a**), light in (**b**) coloration is due to Rhodamine B dye, which is soluble in the ionic layers. Photograph (**a**) was taken in daylight and photograph (**b**) was taken under illumination from uv light (254 nm) (152). See online version for color.

More detailed melting point and glass-transition temperature data are available (38,70,85,89,112,113,153,154), and the IUPAC Ionic Liquid Database (155) will provide a regularly updated on-line source of these data.

8.2. Vapor Pressure. Due to their ionic nature, and fact that their chemical and thermal stability can be designed to be high, ionic liquids can possess a negligibly small vapor pressure, even at high temperatures. Owing to this property, ionic liquids cannot evaporate from the reaction vessel and are retained quantitatively, unlike other industrially used solvents, such as dichloromethane or dimethyl sulfoxide. Therefore, the impact on the environment and the process operation personnel is minimal. It means that volatile products, and even products with conventionally low vapor pressures, can be isolated from ionic liquids by distillation.

However, a negligibly small vapor pressure is not the same as zero vapor pressure, and a 2006 paper (156) reports that many ionic liquids which had been believed to be involatile (such as $[C_nmim][NTf_2]$) can be distilled without decomposition at high temperatures and low pressures (eg, 300°C and 0.1 mbar). Moreover, many ionic liquids where the cation is protonated can be distilled via neutral intermediates (see eqs. 9 and 10) (96,157).

$$[\mathrm{Hmim}]\mathrm{X} \rightleftharpoons \mathrm{mim} + \mathrm{HX} \tag{9}$$

$$[\mathrm{NR_2H_2}][\mathrm{NR_2CO_2}] \rightleftharpoons \mathrm{NR_2H} + \mathrm{NR_2COOH} \rightleftharpoons 2\,\mathrm{NR_2H} + \mathrm{CO_2} \tag{10}$$

Thus, ionic liquids can be designed to be volatile, if that offers a processing advantage.

8.3. Conductivity. Due to their ionic nature, ionic liquids are highly conducting materials (158). In fact, it is this property which historically led to the development of ionic liquids (3), making them ideal candidates for electrochemical applications. Their conductivity, just like other properties, can be fine-tuned by deliberate choice of the anion and cation: both moieties contribute to the conductivity. At present, more studies have been conducted in the first-generation chloroaluminate-based ionic liquids than in the second-generation ones. The specific conductivities of some commonly used ionic liquids are given in Table 1. The conductivity of 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide is higher than that of ethyltrimethylammonium, 1-butyl-1-methylpyrrolidinium (159), or triethylsulfonium analogues (48). Detailed conductivity data are available (48,80,159–162), and those for ionic liquids with protonated cations are especially interesting (162).

8.4. Electrochemical Windows. The electrochemical window is the potential range specific to each ionic liquid in which it is not substantially destroyed by oxidation of the anion or reduction of the cation (158). Typically, the window for ionic liquids is between 3.0 and 6.4 V (70,111–113). Table 2 shows some of the reported electrochemical windows of commonly used ionic liquid solvents, as determined by cyclic voltammetry. All imidazolium-based ionic liquids have a cathodic limit of about −2 V *vs* saturated calomel electrode, and the anodic limit is determined by the nature of the anion. The large electrochemical windows thus obtained, especially for the fluorine-containing anions, show that ionic liquids are ideal candidates not only as solvents and electrolytes for electrochemical redox reactions, but also for battery and fuel cell applications.

Table 1. **Conductivities of Different Ionic Liquids**

Ionic liquid	Conductivity/S cm^{-1}	T/°C	Ref.
$[\mathrm{C_2mim}]\mathrm{Cl}$ - $\mathrm{AlCl_3}$ ($X = 0.44$)	0.0117	29.7	5
$[\mathrm{C_2mim}]\mathrm{Cl}$ - $\mathrm{AlCl_3}$ ($X = 0.50$)	0.0227	30.9	5
$[\mathrm{C_2mim}]\mathrm{Cl}$ - $\mathrm{AlCl_3}$ ($X = 0.67$)	0.0154	32.2	5
$[\mathrm{C_2mim}][\mathrm{BF_4}]$	0.02/0.014	30	113/111
$[\mathrm{C_4py}][\mathrm{BF_4}]$	0.03	30	113
$[\mathrm{C_2mim}][\mathrm{OTf}]$	0.01	20	70
$[\mathrm{C_4mim}][\mathrm{OTf}]$	0.1	150–180	137
$[\mathrm{C_2mim}][\mathrm{O_2CCH_3}]$	0.03	20	70
$[\mathrm{Hmim}][\mathrm{NTf_2}]$[a]	0.00723	25	95
$[\mathrm{C_1Hpyr}][\mathrm{BF_4}]$[a]	0.016	25	65

[a] [Hmim] and $[\mathrm{C_1Hpyr}]$ denote the protonated 1-methylimidazole and 1-methylpyrrolidine cations, respectively.

Table 2. **Electrochemical Windows for Some Common Ionic Liquids**

Ionic liquid	Working electrode	Electrochemical window/V^a	Ref.
$[C_2mim][BF_4]$	Pt	5	163
$[C_2mim][O_2CCH_3]$	Pt	3.8	70
$[C_2mim][OTf]$	Pt	4.1	70,163
$[C_2mim][NTf_2]$	GC	4.1	112
$[C_4mim][BF_4]$	GC	5.45	164
$[C_4mim][PF_6]$	GC	6.35	164
$[C_2mim]Cl$ - $AlCl_3$ ($X = 0.4$)	W	2.8	165
$[C_2mim]Cl$ - $AlCl_3$ ($X = 0.5$)	W	4.4	165
$[C_2mim]Cl$ - $AlCl_3$ ($X = 0.55$)	W	2.9	165
$[P_{6\,6\,6\,14}][NTf_2]$	Ag	5.5	166

^{a}Pt: platinum, GC: glassy carbon, W: tungsten, Ag: silver.

It should be noted here that the presence of traces of water or halides in an ionic liquid decreases both the anodic and cathodic limits, and also influences the diffusion coefficient of dissolved species (167). Furthermore, the choice of electrode plays a role: 1,3-dialkylimidazolium-based ionic liquids have been reported to undergo carbene formation at the surface of platinum-electrodes, while glassy carbon electrodes are inert (164).

The trend of cation stability follows the order of: pyridinium < pyrazolium ≤ imidazolium ≤ sulfonium ≤ ammoniumwhile a series of anions can be arranged in the following order (162):

$$Cl^-, F^-, Br^- < \text{chloroaluminates} \le [BF_4]^-, [PF_6]^-, [AsF_6]^- \le [OTf]^-, [NTf_2]^-, [(C_2F_5SO_2)_2N]^-, [CTf_3]^-$$

8.5. Polarity. Solvents are known to influence the chemical reactivity of a substrate both thermodynamically (eg, position of chemical equilibria) and kinetically (eg, rate constants), due to differences in the solvation of substrates and products and the formation of activated complexes. The solvent polarity is defined as the overall solvation capability of solvents derived from all possible, nonspecific and specific intermolecular interactions between the solute and solvent molecules (168). Interactions thus include dispersive, di- or multipolar, and electrostatic, as well as hydrogen bonding. However, since an overall value of very diverse parameters (such as refractive index, electric permittivity, Hildebrand's solubility parameter, dipole moment, etc) is impossible to establish, ranking of different solvents is generally achieved by comparing the effect of one of their properties to a reference solute. The value of comparing derived polarities of ionic liquids from solvatochromic dye studies with, say, molecular studies is questionable, as the dye environments are so different.

Studies Using Solvatochromic Probes. Given their structure and diversity of functionality, complex solvents such as ionic liquids, which are capable of

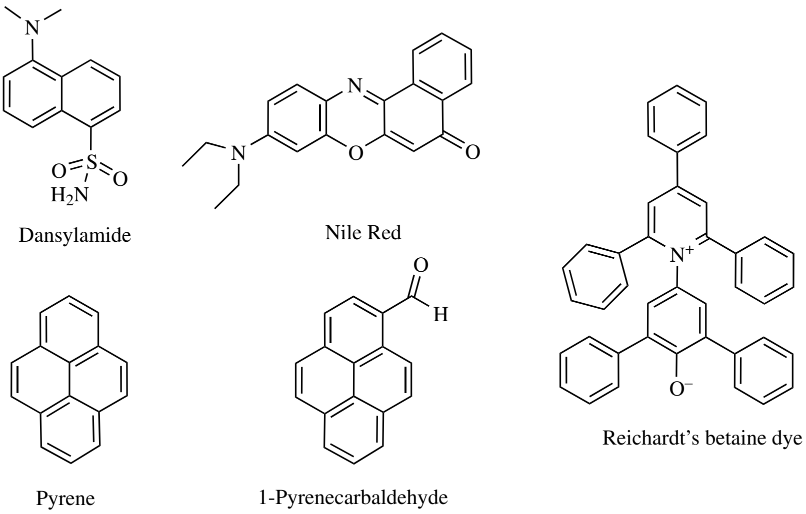


Fig. 10. Some frequently used solvatochromic probes.

multiple types of interactions, are even more difficult to probe than molecular solvents. The first systematic studies were conducted using organic probe molecules in conjunction with spectroscopic techniques (169).

The polarity of $[C_4mim][PF_6]$ with various solvatochromic probes, such as Reichardt's betaine dye, pyrene, dansylamide, Nile Red and 1-pyrenecarbaldehyde (Fig. 10) (170) was investigated. The $E_T(30)$ value obtained with Reichardt's dye indicates a polarity similar to that of ethanol, whereas pyrene and 1-pyrenecarbaldehyde give a higher polarity (similar to ethanenitrile and dimethyl sulfoxide). The Stokes' shift value obtained from the dansylamide probe for $[C_4mim][PF_6]$ is close to the one obtained for ethanenitrile. The positive solvatochromic dye Nile Red, on the other hand, points to a higher polarity of the ionic liquid, which is located between the polarities of 90 wt% glycerol in water and pure water (170).

Keeping this in mind, the studies conducted with one probe can still give useful information about the relative order of a series of homologues. Thus, Seddon and co-workers (169) probed the polarities of some ionic liquids, such as $[C_nmim][NO_3]$ (n = 4–8), $[C_nmim][PF_6]$ (n = 4–8), and $[C_nmim][BF_4]$ (n = 4–10), with the solvatochromic dye Nile Red, and found that they range between methanol and ethanenitrile. These results were confirmed using other solvatochromic probes, such as Reichardt's dye (171) or the 1-(4-oxidophenyl) pyridinium dye (172). Surprisingly, an increase of the alkyl chain length within the $[BF_4]^-$ or $[PF_6]^-$ series revealed that the $[C_6mim]^+$ analogue is more polar than either $[C_4mim]^+$ or $[C_8mim]^+$, although a decrease in polarity over the series is expected. This behavior is not yet understood (169).

It was found that the anion dependent polarity (nucleophilicity) decreases with increasing anion size, probably due to the higher charge delocalization. The polarity decreases therefore in the order of (169):

$$[NO_2]^- > [NO_3]^- > [BF_4]^- > [NTf_2]^- > [PF_6]^-$$

Gordon and co-workers found that the order of nucleophilicities of ionic liquids of a given cation is (172):

$$[OTf]^- > [NTf_2]^- > [PF_6]^-$$

In addition to the lack of a method which measures the overall solvating capacity, variations found between publications using the same probe molecule may be due to differences in the recording technique (emission *vs* absorbance) or solvent purity (170). Also, the polarity was found to increase with decreasing recording temperature, or with increasing water-content in the ionic liquid sample (173). In addition, Rogers and co-workers (174) published a detailed analysis of a solvatochromic dye study, using the Abraham model.

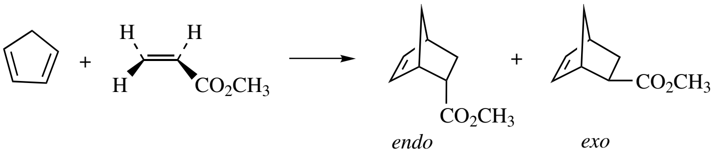
Other Studies. Solvent–solute interactions were studied (175) with the solvation parameter model developed by Abraham, which uses a large number of probe molecules which exhibit various solute–solvent interactions due to acidic, basic, electron-donating, electron-withdrawing, and aromatic functional groups. For this purpose, capillary tubing was coated with various ionic liquids, and the retention of the probes on these gas chromatographic columns was analyzed by multiple linear regression analysis. It was found that the most dominant types of interaction were dipolarity, hydrogen-bond basicity, and dispersion forces. The dispersion forces were very similar for all ionic liquids, but the hydrogen-bond basicity depends mostly on the anion of the ionic liquid. The substitution pattern on the imidazolium cation played a crucial role for the interaction with probes containing nonbonding or π-electron systems. If the substituents are capable of inducing a higher electron density at the ring, stronger interactions with such probes were achieved (175).

The keto-enol tautomerism of pentane-2,4-dione is known to be influenced by the nature of the solvent, and the ratios can be determined using ^{1}H NMR spectroscopy. The equilibrium is dependent on both the concentration and the temperature. The results obtained from various ionic liquids based on the 1-butyl-3-methylimidazolium cation were compared to thirty molecular solvents, and strong correlations with parameters such as reorganization energy, Snyder polarity index and dielectric constant were observed. Data obtained for the dielectric constant suggested that the ionic liquids investigated possess a higher polarity than both methanol and ethanenitrile (176).

In conclusion, these studies suggest that ionic liquids are not as highly polar as they are often assumed to be, but as the results have proven to be technique dependent, the question remains open.

Effect of Polarity on Reactions. In many publications, an effect of the ionic liquid solvent on the rate or selectivity is observed. The following two examples outline how such interactions can be used to govern a reaction, but conclusions relating to polarity arguments must be treated with caution, as there are no reliable data. For example, the biphasic oligomerization of ethene to higher α-olefins in the presence of a cationic nickel complex, which is dissolved in the ionic liquid phase, was influenced by the choice of ionic liquid. During the reaction, the α-olefins (alk-1-enes), which possess a low solubility in $[C_4mim][PF_6]$, are expelled to form a second phase. In contrast, no reaction was observed in butane-1,4-diol, although both solvents showed similar polarities on the E_T scale. On the other hand, probing the solvent basicity indicated that the alcohol has significantly stronger coordination ability than the ionic liquid. It was concluded that the ionic liquid anion interacts less with the catalyst, therefore enabling a higher reaction rate than the alcohol. The low solubility of the products in the ionic liquid leads to the removal of the products from the catalyst solution, which drives the reaction forward, with the added advantage of facile product recovery by simple phase separation (177).

Specific ionic liquid – reactant effects have also been shown to influence the reaction outcome of Diels-Alder reactions, which are known to be dependent on the polarity or solvophobicity of the solvent. Using the model reaction cyclopentadiene and methyl acrylate (eq. 11) in various ionic liquids, Welton and coworkers (178) demonstrated that both the anion and the cation, and thus the polarity of the solvent, played a crucial role.



(11)

If, for example, the acidic proton in the C-2 position in $[C_4mim][BF_4]$ was substituted with a methyl group ($[C_4dmim][BF_4]$), the *endo*-selectivity dropped significantly. The authors propose that the hydrogen-bond donor ability of the solvent is responsible for this effect. This theory is further enhanced by the fact that N-H or O-H hydrogen bond donor sites in functionalized ionic liquids also increase the *endo*-selectivity (178). The *endo/exo* ratio decreased when the reactions were carried out in $[C_4mim]^+$ homologues in the order of:

$$[ClO_4]^- = [PF_6]^- > [BF_4]^- > [OTf]^- > [NTf_2]^- > [CF_3CO_2]^-$$

thus following approximately the decrease in the polarity (178).

8.6. Viscosity. For imidazolium-based cations, the viscosity of ionic liquids is dependent on the alkyl chain length of the cation, as well as the nature of the anion. The viscosity of the $[BF_4]^-$ series with increasing temperature is shown in Figure 11.

It is obvious that the viscosity increases with increasing alkyl chain length, due to the increased possibility of van der Waals-type interactions between the cations. Ionic liquids with short chains ($n < 12$) exhibit Newtonian behavior (ie, the viscosity is independent of the shear rate) (179), whereas those derivatives that exhibit liquid crystalline phases (see Section 8.1) show non-Newtonian behavior. These compounds give curves with abrupt discontinuities; at lower temperatures, their viscosity is high, due to their order, which, with increased temperature, is disrupted. This leads to the formation of a liquid crystal mesophase, which turns into an isotropic ionic liquid at even higher temperatures.

Besides the length of the alkyl chain, the symmetry of the anion, its molar mass and the ability to form hydrogen bonds all influence the viscosity (138).

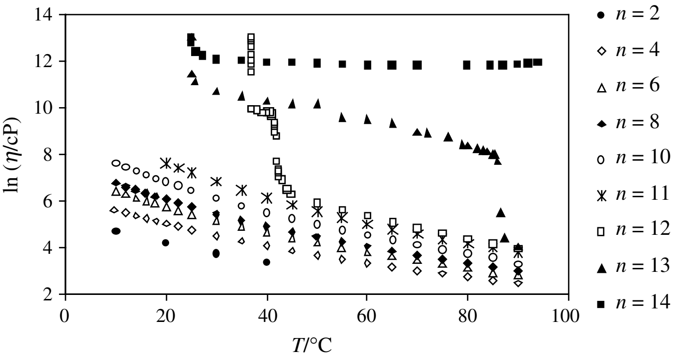


Fig. 11. Viscosities of [$C_n$mim][BF_4] ($n = 2$ to $n = 14$) *vs* temperature (179).

Selected data are given in Table 3, and further data have been published (48,80,138,159,160,180–182).

The viscosity of second-generation ionic liquids ranges from between 20 to 2000 cP, which appears to be quite high from an engineering point of view. However, upon addition of organic solvents with varying properties, the viscosity of any ionic liquid decreases dramatically, even if present in quantities <10 mol% (32). This phenomenon is illustrated in Figure 12 by the example of [C_4mim][BF_4]. For the practical application of a very viscous ionic liquid as a solvent this is advantageous, as the viscosity may be lowered by the addition of reactants, thus facilitating some engineering aspects.

The decrease in viscosity can be easily predicted using eq. 12:

$$\eta = \eta_s \exp\left(-X_{cs}/a\right) \tag{12}$$

Table 3. **Selected Viscosity Data for Various Ionic Liquids**

Ionic liquid	Viscosity/cP	Temp./°C	Ref.
[C_2mim][BF_4]	66.5	20	32
[C_2mim][PF_6]	23.4	70	32
[C_2mim][OTf]	50.0	20	32
[C_2mim][NTf_2]	34	20	183
[C_4mim]Cl	1534	50	32
[C_4mim][BF_4]	154	20	32
[C_4mim][PF_6]	371	20	32
[C_6mim]Cl	1124	50	32
[C_6mim][BF_4]	314	20	32
[C_6mim][PF_6]	690	20	32
[C_8mim]Cl	1930	50	32
[C_8mim][BF_4]	439	20	32
[$P_{6\,6\,6\,14}$]Cl	~1500	25	166

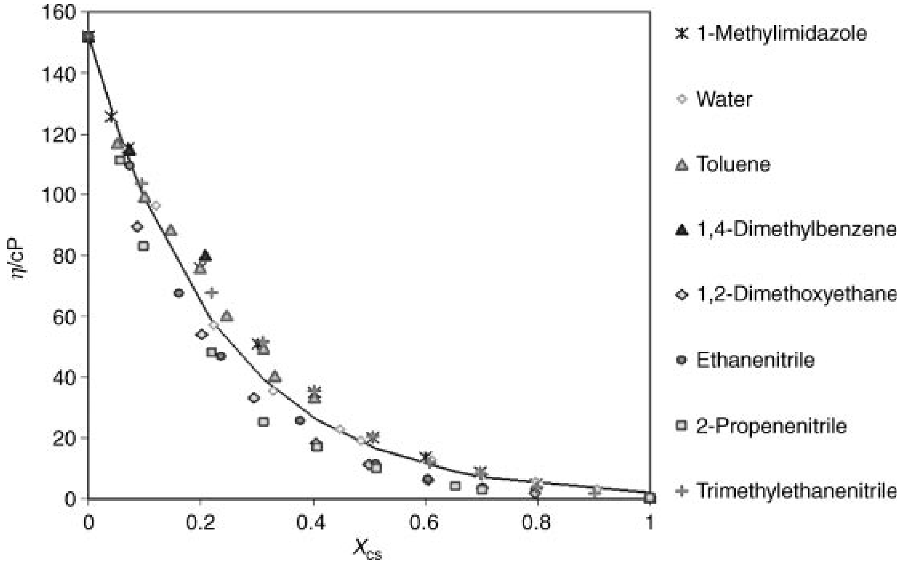


Fig. 12. Viscosity (at 20°C) of molecular solvent - $[C_4mim][BF_4]$ mixtures, where X_{cs} is the mole fraction of added organic solvent (32).

where η_s is the viscosity of the pure ionic liquid, X_{cs} is the mole fraction of the molecular solvent, and a is a constant value specific to each ionic liquid (ie, $\alpha = 0.23$ for $[C_4mim][BF_4]$ and 0.19 for $[C_4mim][PF_6]$) (32).

Nevertheless, one of the future challenges of ionic liquid research is to reduce the viscosity of ionic liquids by at least one order of magnitude.

8.7. Density. The density of $[C_n mim]^+$- and $[C_n py]^+$-based ionic liquids containing inorganic anions such as $[BF_4]^-$ or $[PF_6]^-$, is higher than that of water, ie, if one of these ionic liquids is immiscible with water, it will form the heavier, lower phase. Within a homologous series, eg, $[C_2\text{-}C_{10}mim][BF_4]$, the ionic liquids with shorter alkyl chain possess higher densities than the ones with longer chains (see Fig. 13).

This can be explained by the ability of the shorter alkyl chain analogues to close-pack and therefore achieve a higher density, whereas the bulkiness of the longer chain derivatives leads to less efficient close-packing (179). Although no such data are available at present, Figure 13 shows that theoretically, imidazolium-based ionic liquids with densities <1 g cm^{-3} are conceivable, if the alkyl chain length and temperature are increased. If water-immiscible, such ionic liquids would form the lighter phase of a water-ionic liquid biphasic system. Recently, it has been observed that phosphonium-based ionic liquids possess very low densities: at 30°C, the density of trihexyltetradecylphosphonium chloride is 0.88 g cm^{-3}, while that of the corresponding $[BF_4]^-$ was found to be 0.93 g cm^{-3} (166). In contrast, the density $[C_2mim]Br\text{-}AlBr_3$ ($X = 0.5$) is >2.4 g cm^{-3} at 22°C (184). Thus, a large range of densities is covered by ionic liquids, and this could be easily extended by design.

Selected density data are given in Table 4, and further data are available in the literature (48,80,138,159–161,179,180,185).

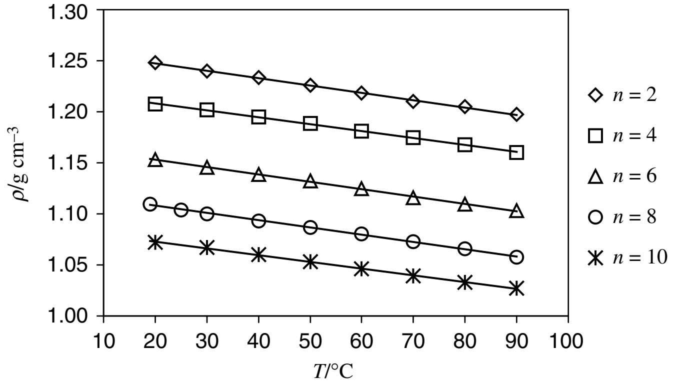


Fig. 13. Density of $[C_n\text{mim}][BF_4]$ ($n = 2$ to $n = 10$) *vs* temperature (179).

8.8. Refractive Index. It is known that the refractive index decreases with increasing temperature, or increasing concentration of a solution. It can therefore be utilized to quantitatively determine the concentration in mixtures and monitor purity (188,189).

Table 5 shows that the refractive index linearly increases with increasing alkyl chain for a given cation type. Of more importance, however, is the ability to design ionic liquids with high refractive indices, significantly higher than can be achieved with organic molecular solvents. Guided by the parachor (190), Deetlefs and co-workers created novel ionic liquids to permit the refractive indices of gems and minerals to be measured safely, without exposing the researchers to noxious fumes (188).

8.9. Water Solubility and Effect on Physical Properties. The solubility of water in ionic liquids is strongly influenced by their composition and in particular by the nature of the anion. Hydrophobic ionic liquids are usually based on fluorinated anions, most commonly $[PF_6]^-$, $[OTf]^-$, $[NTf_2]^-$ and $[BF_4]^-$. Tetraalkylammonium tetraalkylborates form biphasic systems with

Table 4. **Selected Density Data for Various Ionic Liquids**

Ionic liquid	Density/g cm^{-3}	Temp./°C	Ref.
$[C_4\text{mim}][PF_6]$	1.37	20	186
$[C_4\text{mim}]Cl$	1.08	25	138
$[C_4\text{mim}][BF_4]$	1.17	30	186
$[C_2\text{mim}][OTf]$	1.39	22	70
$[C_6\text{mim}][PF_6]$	1.29	25	138
$[C_6\text{mim}]Cl$	1.03	20	138
$[C_6\text{mim}][BF_4]$	1.15	20	32
$[C_8\text{mim}]Cl$	1.00	25	138
$[C_8\text{mim}][BF_4]$	1.08	40	187
$[P_{6\,6\,6\,14}]Cl$	0.88	30	166
$[P_{6\,6\,6\,14}][BF_4]$	0.93	30	166

Table 5. **Refractive Indices for Various Ionic Liquids at 20°C**

Ionic liquid	Refractive index	Temp./°C	Ref.
$[C_4py][BF_4]$	1.446	20	191
$[C_6py][BF_4]$	1.449	20	191
$[C_4mim][BF_4]$	1.422	20	191
$[C_6mim][BF_4]$	1.429	20	191
$[C_8mim][BF_4]$	1.433	20	191
$[C_4dmim][BF_4]$	1.434	20	191
$[C_6dmim][BF_4]$	1.438	20	191
$[C_8dmim][BF_4]$	1.442	20	191
$[C_4mim][PF_6]$	1.409	25	138
$[C_8mim][PF_6]$	1.423	25	138
$[C_2mim][NTf_2]$	1.423	20	70
$[C_4mim][NTf_2]$	1.427	20	70
$[C_2mim][OTf]$	1.433	20	70
$[C_4mim][OTf]$	1.438	20	70
$[C_4mim][I_3]$	1.700	20	188
$[C_4mim][I_5]$	1.910	20	188
$[C_4mim][I_7]$	1.950	20	188
$[C_2mim][I_7]$	2.010	20	188
$[C_2mim][I_9]$	2.080	20	188

water (108,192), but are only moderately stable in air and have therefore not been used recently (27). The properties of the cation play a role as well, albeit somewhat subordinate: the hydrophobicity of a homologous series, for example $[C_nmim][BF_4]$, increases with increasing alkyl chain length, so that $[C_nmim][BF_4]$ ($n = 2–5$) are fully miscible with water at room temperature, but the higher derivatives are not (85). Similarly, all reported second-generation ionic liquids based upon $[P_{66614}]^+$ are hydrophobic too (166). $[C_nmim][OTf]$ with $n > 4$ (137) or $[NTf_2]^-$ (54) also give water-immiscible ionic liquids. On the other hand, all $[C_nmim][PF_6]$ ionic liquids are hydrophobic and form biphasic systems with water (150,153), even at room-temperature.

Solubility is, as would be expected, also dependent on the temperature. Thus, $[C_4mim][BF_4]$ is miscible with water at ambient temperature; however, phase separation can be achieved at temperatures <5°C (186). This phenomenon has been used to advantage: in the rhodium-catalyzed hydrogenation of polar alkynes, $[C_8mim][BF_4]$, water, the starting material and the product mix to give a homogeneous phase at 80°C and 60 bar, which phase-separates upon cooling (193).

It should be noted that although ionic liquids that form biphasic systems with water are often referred to as "hydrophobic ionic liquids", but they **DO** dissolve water to some extent and are often hygroscopic. Figure 14 shows the amount of water soluble at room temperature in tetrafluoroborate and hexafluorophosphate ionic liquids upon equilibration, even though all of them form biphasic systems with an excess of water (32). The amount of water soluble in the

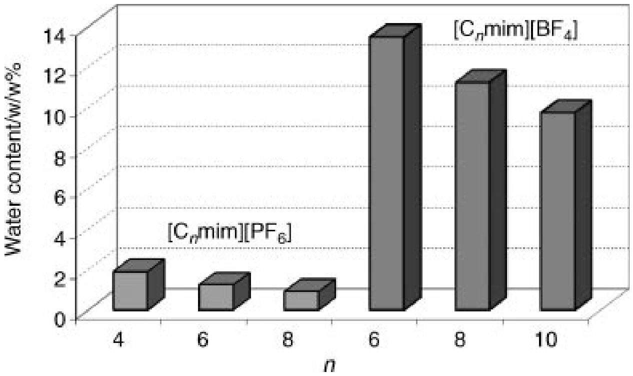


Fig. 14. Saturated water solubilities in [$C_n$mim][PF_6] ($n = 4–8$; blue) and [$C_n$mim][BF_4] ($n = 6–10$; red) at room temperature (32). See online version for color.

[PF_6]$^-$ series is notably smaller than in the [BF_4]$^-$ series, and decreases with increasing chain length.

Another important feature of these hydrophobic ionic liquids, the extent of their hygroscopicity, is shown in Figure 15. The diagram shows the up-take of atmospheric water into [C_4mim][BF_4] and [C_4mim][PF_6] over three hours while stirring at room temperature and ambient pressure, determined by Karl-Fischer titration (32). During this interval, significant amounts of water are absorbed into the ionic liquid phase, which decreases the viscosity of the ionic liquids. It is interesting to note that [C_4mim][BF_4] is more hygroscopic than [C_4mim][PF_6], and both ionic liquids do not reach saturation within the time scale. In a similar water-absorption study, the water-uptake of the [BF_4]$^-$

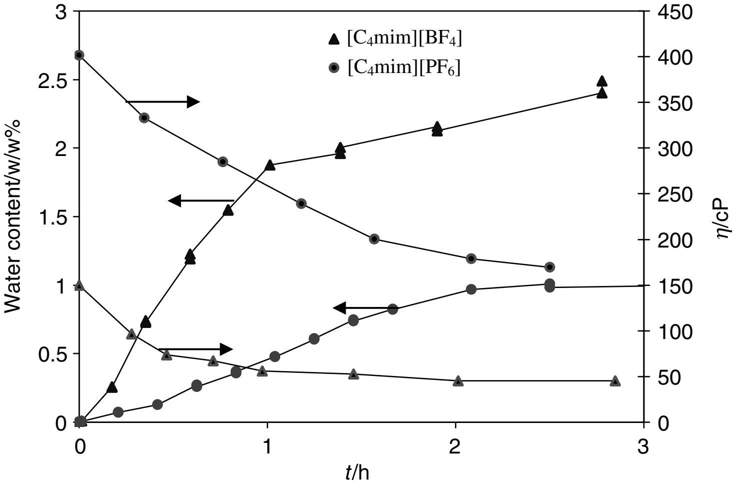


Fig. 15. Water-uptake (blue, left hand axis) from the atmosphere within 3 h in [C_4mim][BF_4] (triangles) and [C_4mim][PF_6] (circles) compared to its influence on viscosity (red, right hand axis) (32). See online version for color.

homologue was found to initially proceed slower than for the $[NTf_2]^-$ and $[PF_6]^-$ ionic liquids, which was attributed to its relatively higher viscosity (194).

Although hygroscopicity would be expected for ionic liquids containing anions with strong tendency of forming hydration shells (eg, halides), it is rather surprising to find that ionic liquids containing anions with relatively low coordination ability such as $[NTf_2]^-$ or $[PF_6]^-$ exhibit this property. The driving force for this absorption must be related to a change of internal order, leading to a more favorable structure of lower energy. The physico-chemical properties of ionic liquids, such as their solubility, polarity, conductivity and viscosity are altered by the amount of water absorbed. This will change the rates of chemical reactions and efficiencies when ionic liquids are used as solvents in reaction. In catalytic reactions, for example, the coordination ability of a solvent with a catalyst is known to influence the efficiency of the catalyst. Also, traces of water present will influence the solubility of other substances in the ionic liquid medium. As an example, the solubility of carbon dioxide was first underestimated, as no precautions were taken to exclude traces of water in the ionic liquid (187).

Interestingly, unlike the viscosity (which drops rapidly upon addition of a cosolvent), the density is less affected as long as there is a molar excess of ionic liquid present. Figure 16 shows the dependence of both the density and viscosity of $[C_4mim][BF_4]$ on the water content. In contrast, when ($X_{IL} < 0.5$, where X_{IL} = molar fraction of ionic liquid), the density rapidly decreases towards that of pure water (32). From a philosophical aspect, this means that when $X_{IL} > 0.5$, the context is a solution of water in an ionic liquid; when $X_{IL} < 0.5$, it is an aqueous solution of an ionic liquid.

In conclusion, the ability to absorb water from the atmosphere is a critical issue: although these second-generation ionic liquids may be used on the bench top, extreme care must be taken to avoid absorption and accumulation of water. Even when the ionic liquid investigated is water immiscible, it needs to be thoroughly dried, and handled in a dry-box, or under a dry dinitrogen or argon atmosphere.

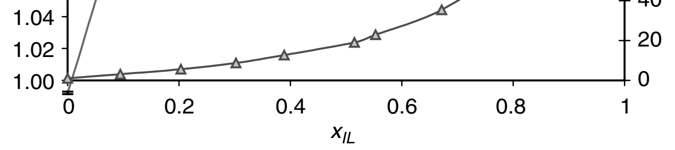


Fig. 16. Density (squares) at 40°C and viscosity (triangles) at 20°C of $[C_4mim][BF_4]$–water mixtures *vs* molar fraction of $[C_4mim][BF_4]$ (32).

Some detailed data concerning water solubility on equilibration of hydrophobic ionic liquids, and its influence on properties such as the melting point, glass-transition temperature, thermal decomposition temperature, viscosity, surface tension, and density have been reported (138,195). The structures of water-ionic liquid mixtures have been examined spectroscopically, and this is discussed in Section 10.3 (103).

8.10. Solubility in Ionic Liquids. Ionic liquids can be designed to dissolve most materials (such as polymers, organic and inorganic compounds, and transition metal catalysts) to a higher degree than conventional solvents (28). This may lead to process intensification, since a smaller reactor volume implies less energy for heating to reaction temperature or cooling (82). In one approach, the solubility of a reactant and product can be fine-tuned by alteration of the lipophilic character of the ionic liquid, eg, by increasing the alkyl chain length. In this way, biphasic systems can be obtained, in which the catalyst is dissolved in the ionic liquid, while the product forms a second layer (15). Thus, the advantages of homogeneous catalysis are sustained, and the catalyst and solvent are easily recycled by simple phase separation.

Some data for the solubilities of alkenes in ionic liquids are beginning to appear in the literature (30,128,177,196–198). Generally speaking, it can be concluded that lengthening the alkyl chain of alkenes leads to a decrease in solubility in a given ionic liquid (eg, 0.110 g ethene per g $[C_4mim][PF_6]$ vs 0.002 g oct-1-ene per g $[C_4mim][PF_6]$) (177), which can be attributed to the increase of the nonpolar character of these substrates. Likewise, if the alkyl chain length on the cation of the ionic liquid is increased, the solubility of a given non-polar organic substrate, such as an alkene, increases (eg, 0.158 g oct-1-ene per g $[N(C_4H_9)_3CH_3][4\text{-}CH_3C_6H_4SO_3]$, vs 0.382 g oct-1-ene per g $[N(C_6H_{13})_3CH_3][4\text{-}CH_3C_6H_4SO_3]$ (30). The solubility of a polar molecule such as water, on the other hand, decreases in such a case (Fig. 14).

It is often difficult to correlate the influence of the anion of the ionic liquid with the solubility of a given substrate. Olivier-Bourbigou and co-workers (198) found that the solubility of hex-1-ene increases for the same cation, eg, $[C_4mim]^+$, as follows:

$$[BF_4]^- < [PF_6]^- < [OTf]^- < [CF_3CO_2]^- < [NTf_2]^-$$

Similarly, the solubility of alcohols increases in the following order (199):

$$[PF_6]^- < [BF_4]^- < [NTf_2]^- < [OTf]^- < [N(CN)_2]^-$$

These findings correspond approximately to the trends established for the polarity.

Blanchard and Brennecke (197) measured the solubility of different solid and liquid organic substrates in $[C_4mim][PF_6]$ at ambient temperature and pressure, and found that in general, solids were less soluble than liquid organics. The data in this paper for hexane are misreported; hexane is essentially insoluble in the ionic liquids studied (200). The solubility of substances with the potential for strong intermolecular interactions (eg, those exhibiting a large dipole moment) is higher than that of non-polar molecules. Also, aromatic substances are soluble to a higher degree than non-aromatic compounds of equivalent molecular weight and polarity (197).

When two molecular solutes are present, several ternary phase diagrams have been determined, especially for ionic liquid + water + alcohol mixtures (201–204) and ionic liquid + ethanol + (1,1-dimethylpropyl ethyl ether) (205). In general, lengthening the alkyl chain substituent on the ionic liquid cation leads to an increase of alcohol solubility (203). For a given ionic liquid, the solubility of a series of alcohol homologues decreases with increasing alkyl chain length (199,204). In the three-component system, the presence of alcohol increases the solubility of water in the ionic liquid, up to a molar ratio of 1:1 (alcohol:water). Thus, this ratio can be used as a tool to fine-tune the solubility, so that either total or partial solubility or essentially complete phase separation can be achieved (202).

Relatively little data for gas solubilities are available at present. In general, the solubility of gases increases with increasing pressure, and decreases with increasing temperature (187,206). The group of Brennecke investigated the solubility of CO_2, CO, CH_4, N_2, and H_2 in $[C_4mim][PF_6]$ at 25°C at pressures up to 13 bar. The solubility of CO_2 (20 mole% at 10 bar) is considerably greater than that of the other gases (less than 5 mole%). The Henry's law constants obtained are: 50 bar for CO_2, 190 bar for CH_4, 303 bar for CO, 281 bar for N_2 and 353 bar for H_2 (207).

Measurements conducted by Dupont and co-workers (208) give Henry coefficients of 0.003 mol l^{-1} bar^{-1} H_2 for $[C_4mim][BF_4]$ and 0.00088 mol l^{-1} bar^{-1} for $[C_4mim][PF_6]$. These values indicate that gas solubilities are dependent on the type of anion of the ionic liquid (209), which has been shown to have implications in the outcome of reactions: in asymmetric hydrogenations, for example, a higher solubility of dihydrogen leads to higher enantiomeric excesses as well as higher conversions (209).

Detailed investigations in $[C_4mim]^+$-based ionic liquids have shown that at 25°C, the solubility of CO_2 increases (see also Fig. 17) in the following order (210):

$$[NO_3]^- < [N(CN)_2]^- < [BF_4]^- \sim [PF_6]^- < [OTf]^- < [NTf_2]^- < [CTf_3]^-$$

For a given anion, the increase of the alkyl chain substituent on the 1-alkyl-3-methylimidazolium cation also increases the CO_2 solubility slightly (206), while the introduction of a methyl substituent in the C-2 position decreases its solubility (Fig. 17) (210).

The solubility of carbon monoxide was determined using high pressure NMR spectroscopy (211). It increases in the order:

$$[BF_4]^- < [PF_6]^- < [SbF_6]^- < [OTf]^- < [NTf_2]^-$$

Similar to the trend observed for carbon dioxide (210), and a longer alkyl substituent on the cation also improves the solubility (211).

Moisture present in the ionic liquid decreases the CO_2-solubility (212). Since the ionic liquid does not dissolve in the CO_2-phase, as opposed to conventional organic liquids, cross-contamination and leaching are not encountered, so

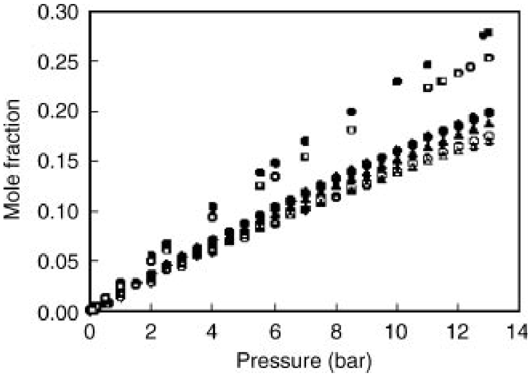


Fig. 17. Solubility of CO_2 in [C_2mim][NTf_2], ■; [C_2dmim][NTf_2], □; [C_4mim][PF_6], •; [C_4dmim][PF_6], ○; [C_4mim][BF_4], ▲; [C_4dmim][BF_4], △ at 25°C. Reprinted with permission from (210). Copyright (2004) American Chemical Society.

that CO_2 can be used for the extraction of products from the ionic liquid phase (see Section 11.1) (212).

9. Handling, Safety and Toxicology

When working with the *first-generation* ionic liquids, close attention needs to be paid to the materials of containment, since low-density as well as high-density polyethenes are decomposed at temperatures >100°C (23). To the best of current knowledge, most *second-generation* ionic liquids based on anions other than $[PF_6]^-$ and $[BF_4]^-$ are stable in the presence of water and dioxygen. $[PF_6]^-$-based ionic liquids have been found to etch glass in the presence of traces of water (144) at elevated temperatures, due to the formation of toxic HF. The use of such ionic liquids is thus being phased out (see Section 7.2). Additionally, residual halide impurities, from the preparation of the ionic liquid (see Section 5), may corrode metal vessels (114), so that high-grade stainless steel, Hastelloy, Teflon, or glass equipment should be used. Recently two papers reporting detailed corrosion studies of a range of metals in ionic liquids, both at room temperature (213), and at elevated temperatures (214), have appeared – studies at higher temperatures offered clear evidence of significant corrosion, especially for copper and brass.

In laboratory experiments, standard glassware is generally used, and for autoclave work a glass or Teflon lining is recommended, especially for the preparation of hexafluorophosphate or tetrafluoroborate ionic liquids.

Very little is presently known about the environmental behavior, safety and health issues (eg, flammability/compatibility) and disposal strategies for ionic liquids, although an environmental risk assessment strategy for toxicity determination has been outlined (215). Pernak and co-workers (216) assessed the acute oral toxicity of the ionic liquid 3-hexyloxymethyl-1-methylimidazolium tetrafluoroborate by the Gadumm method, and found that the $LD_{50} = 1400$ mg kg^{-1} for female and the $LD_{50} = 1370$ mg kg^{-1} for male Wistar rats. [C_2mim]Cl was found to possess a low aquatic toxicity (*daphnia magna*: $EC_{50} > 100$ mg l^{-1}), and its potential for bioaccumulation is low log(K_{OW}: −0.31). However, these results also indicate a poor biodegradability (217).

Although some biocatalytic processes using enzymes have been reported to proceed well in the presence of ionic liquids (see Section 11.4), acetylcholinesterase was found to be increasingly more inhibited with lengthening of the alkyl-substituent on the 1,3-dialkylimidazolium cation. As for the type of cation, phosphonium and pyridinium derivatives were less inhibitory than imidazolium-based ionic liquids (218).

The marine bacterium *Vibrio fischeri*, as well as two rat cell types, were exposed to dialkylimidazolium-based ionic liquids. While the bacterium luminescence was not influenced by the choice of anion, a stronger inhibition of luminescence was found for derivatives with longer alkyl substituents, which also decreased the cell viability of mammalian cells, and therefore the EC_{50} (219). However, the effect concentrations of the test systems were lower than the toxicity of solvents such as propanone, ethanenitrile, methanol or methyl *t*-butyl ether (219). The soil roundworm *caenorhabditis elegans* was used to test the toxicity of various 1-alkyl-3-methylimidazolium chlorides. Again, the lethality increased with the length of the alkyl substituent (220).

Alkoxy-substituted ionic liquids display anti-microbial activity against cocci, rods and fungi. The alkyl chain length greatly affected these activities: shorter substituents render the ionic liquid less active, while substituents with 10-14 carbon atoms in the alkoxy-group gave rise to very high anti-microbial activities. On the other hand, relatively little influence of the anion was found (221). Using the "Closed Bottle Test" (OECD), it was found that ester-functionalized ionic liquids such as 3-methyl-1-(alkyloxymethylcarbonyl)-imidazolium bromides biodegrade more easily than 1,3-dialkylimidazolium derivatives (222).

Concluding from these studies, it appears that the higher toxicity of longer chain alkyl-substituted derivatives is related to an increased hydrophobicity which allows for the permeation of the ionic liquid into the cell membrane.

No data have been published on the procedures for the safe disposal of ionic liquids. However, recently a study of the adsorption of [C_4mim]Cl onto bacterial and mineral surfaces, such as the Gram-positive soil bacterial species *bacillus subtilis*, gibbsite, quartz and Na-montmorillonite, was conducted to elucidate the fate and transport in environmental systems. The results suggest that the geologic retardation of this ionic liquid will occur if interlayer clays are present in the subsurface, but little interaction with other common surfaces occurs. Therefore, the mobility of this ionic liquid, once reaching the water table, is expected to be high and viable disposal strategies should be devised (223).

Overall, although there are a scattering of reports on these important areas, there are no published comprehensive studies, and these are urgently needed, as is a design strategy for preparing ionic liquids of low toxicity with excellent biodegradability.

10. Structural Studies

10.1. Pure Ionic Liquids. There is very little known about the structure of pure ionic liquids, mainly owing to the fact that these compounds are noncrystalline over a wide temperature range (85), making it difficult to obtain crystal structures. As indicated in Section 8.1, the melting point is lowest for the 1-alkyl-3-methylimidazolium salts of medium alkyl chain length, and therefore only crystal structures of ionic liquids with either short or extremely long ($n > 10$) alkyl chains have been obtained. The few crystal structures of short chain homologues available show that hydrogen bonding between the anions and cations can occur to varying degrees, if the anion is nucleophilic (eg, halides) (224); the cationic ring C-H protons are significant hydrogen-bond donors.

Long-chain 1-alkyl-3-methylimidazolium salts have been studied by various techniques, and the phase behavior was found to be much more complex (eg, liquid crystal polymorphism, amphiphilicity, etc) than that of imidazolium salts with shorter alkyl chains (78,151,225,226). Although the compounds from which crystal structures were derived are formally very similar to such compounds that are liquid at room temperature, it is questionable if predictions of the structure in liquid state can be made from data derived in the solid state.

In 2003, several groups published their results on the structure of pure ionic liquids containing the $[C_4mim]^+$ cation (227–230). The techniques used included Raman spectroscopy, X-ray crystallography and X-ray powder diffraction. $[C_4mim]Cl$, a solid at room-temperature, was found to possess at least two polymorphs, one being a metastable form of the other. Both cation conformations coexist in the super-cooled liquid state. Interestingly, $[C_4mim][BF_4]$, a liquid at room temperature, gave a similar Raman spectrum as the mixture of both polymorphs of $[C_4mim]Cl$, indicating that both structures may coexist also in the liquid state. The authors suggested that polymorphism is not dependent on the type of anion present (227).

The two polymorphs of $[C_4mim]Cl$ structurally differ in the angle in which the butyl moiety protrudes from the imidazolium plane. In crystals of type 1 (Fig. 18**a**), the chloride is hydrogen bonded to the C-2-hydrogen and to two C-7-methene hydrogens of different cations. The interactions with the other ring hydrogen atoms or the methyl moiety is negligible. Such a crystal features channels, in which the chloride anions are accommodated (228,229). In the metastable $[C_4mim]Cl$ crystals of type 2 (Fig. 18b), on the other hand, the interaction of chloride with the C-4 and C-5 hydrogens is much more pronounced. Such crystals can only be obtained when a second solvent or solute species is present during crystallisation.

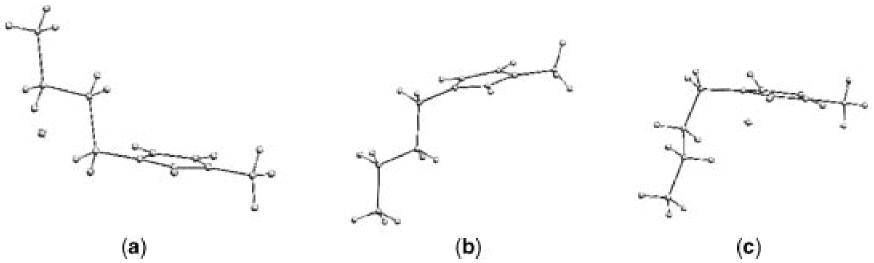

(a) (b) (c)

Fig. 18. Structures of the cations from the two polymorphs of $[C_4mim]Cl$ [type 1 (**a**) (228), type 2 (**b**) (229)], and from the type 2 polymorph of $[C_4mim]Br$ (**c**) (229,230).

Both structures represent minima of the potential surface energy, and give distinctive crystals. The formation of a "eutectic" liquid region below the melting point of both polymorphs can be anticipated. It is interesting to note that although the type 1 crystal was the thermodynamically stable polymorph of [C_4mim]Cl, [C_4mim]Br preferably crystallizes as a type 2 polymorph (Fig. 18**c**) (229,230).

NMR spectroscopy is another tool to study structural arrangements in the liquid or solid state. For [C_2mim][BF_4], a strong dependence of the hydrogen bonding between the ions on the temperature was observed. It was found that, below 24°C, the ions behave in a "*quasi*-molecular" manner, as discrete ion pairs. At higher temperature, this strong anion-cation interaction was disrupted, and individual ions are present, which may participate in an extended hydrogen-bonded network (231).

The liquid structure of ionic liquids can best be determined by analyzing neutron diffraction data obtained at various temperatures below 100°C to an empirical potential structure refinement process. Liquid structures are then compared to solid state structures from crystallographic experiments. The solid structures of [C_1mim]Cl and [C_1mim][PF_6], both containing the symmetrical 1,3-dimethylimidazolium cation, show strong similarities, where adjacent cations are hydrogen bonded to one another *via* $CH_3 \ldots \pi$ interactions in a dimeric fashion. Differences stem from the variation in anion size and hydrogen-bonding ability, leading to both different packing of the dimers and an expansion of the liquid network of the $[PF_6]^-$ salt (232,233). The results obtained by this method for liquid [C_1mim]Cl and [C_1mim][PF_6] are in good agreement with their crystal structures (232), as well as with results obtained by molecular dynamics calculations (234). Similar radial distribution functions are found in both salts, and the larger first shell anion-cation distance in the hexafluorophosphate salt is also consistent with its crystal structure. Due to the high hydrogen-bonding ability of the chloride salt, the H-2 of the cation was the most likely position of interaction. On the other hand, the hexafluorophosphate anions are most likely positioned above or below the imidazolium ring (Coulombic forces), and little interaction occurs axial to the H-2 proton. Although such an anion-cation stacking had been proposed (235), other experimental data (from IR and NMR spectroscopy) indicates that the hexafluorophosphate anion preferably interacts with the H-2 hydrogen, similarly to the chloride anion, albeit less pronounced. The cation-cation distribution in the chloride salt showed an even distribution for the chloride salt. On the other hand, essentially no cation-cation interaction was found to exist in the $[PF_6]^-$ homologue, due to the $[PF_6]^-$ anion obstructing the space facing the imidazolium ring at high probability. The authors concluded that with the exception of the deviation at high probability, the liquid and solid-state structures of [C_1mim][PF_6] and [C_1mim]Cl are very similar (232,233).

10.2. Ionic Liquid-Cosolvent Mixtures. Ionic liquid/CO_2 mixtures were investigated at high pressures and elevated temperatures using attenuated total reflectance (ATR) infra-red spectroscopy. It was found that the dissolved CO_2 interacts with the anions of the ionic liquids ([C_4mim][BF_4] or [C_4mim][PF_6]), with the axis of the O=C=O molecule perpendicularly orientated towards the P-F or B-F bonds. The interaction with the tetrafluoroborate was stronger than with the hexafluorophosphate, indicating that the former anion acts as a stronger Lewis base towards CO_2 (236).

Harper and Lynden-Bell have used molecular dynamics simulations to model binary mixtures of aromatics and 1,3-dimethylimidazolium hexafluorophosphate. In addition to the large cation-anion interactions exhibited by the ions of the ionic liquid, structural effects of such mixtures are strongly dependent on the local electrostatic field of the solute: although benzene is sterically similar to hexafluorobenzene, the former was found to have the 1,3-dimethylimidazolium cations preferably arranged above and below its plane, with the anions positioned in the equatorial regions. In mixtures with hexafluorobenzene, on the other hand, the cations are arranged around the equator of the solute, whereas the anions are positioned above or below the plane. This effect is ascribed to the larger negative charge around the equator, and the relative positive charge on the poles, of hexafluorobenzene. Surprisingly, this microscopic description did not change upon further dilution with the aromatic solute. Another interesting finding was that in both the benzene–ionic liquid and the hexafluorobenzene–ionic liquid mixtures, the interactions between the ions located above or below the solute plane (ie, the cations and the anions, respectively) are repulsive rather than attractive. It is the ions arranged in the equatorial region which exhibit strong Coulombic and total attractive energies. The authors predict that such selective interactions of the solute with either the cation or the anion will have an effect on the reaction outcome when carried out in such a system (237).

Another interesting type of interaction between some ionic liquids and aromatic organic substrates (eg, benzene, toluene or xylene) is the formation of clathrates (liquid inclusion compounds), first observed decades ago by Atwood (238). Many aromatics have a remarkably high solubility in ionic liquids of the 1-alkyl-3-methylimidazolium type, but in most instances phase separation occurs at high concentrations of the substrate. In such clathrates, the cation-anion interactions of the pure ionic liquids is disturbed by the presence of the aromatic compound, and a new internal structure, based on associative interactions between the aromatic compound and the salt ions, is formed. An energetic equilibrium between the forces driving the crystallisation of the pure salt (eg, cation-anion association) and the solvation interactions of the ions with the aromatic compound must exist to obtain a stable clathrate. Such liquid clathrates exhibit low viscosities (as compared to the pure ionic liquid), and constant, but nonstoicheiometric, compositions (239). In one instance ($[C_1mim][PF_6]$), it was possible to crystallize and analyze such an inclusion compound with a ratio of ionic liquid:benzene of 1:2. The crystal exhibits a three-dimensional array of hydrogen-bonded cations and anions, which results in the formation of channels, in which the benzene molecules are accommodated. Although a strong π-π interaction between the benzene molecules should be expected, this interaction is substituted by π-π interactions with the imidazolium cations, which sandwich each benzene molecule, as predicted from molecular dynamics simulations (237). The existence of such inclusion compounds highlights yet again the importance of understanding the interactions possible in ionic liquids. For example, when reactions involving aromatic compounds are carried out in an ionic liquid, this phenomenon will have a strong impact on the separation of the product from the solvent, and possibly on the reactivity of the aromatic compound as well. Furthermore, it can be predicted that ionic liquids may be used to favorably influence the separation of aromatics from aliphatic compounds (239,240).

10.3. Ionic Liquid–Water Mixtures. Near-infra-red (NIR) spectrometry has been used as a noninvasive and *in situ* probe to investigate the states of water in the ionic liquids [C_4mim][BF_4], [C_4mim][PF_6], and [C_4mim][NTf_2]. Three different water species were detected in the [PF_6]$^-$ and [NTf_2]$^-$ ionic liquids, but no assignment to specific structures could be made. However, it can be stated that the hydrogen bonds formed were strongest in the [BF_4]$^-$ and weakest in the [PF_6]$^-$ ionic liquid (194).

In voltammetric studies, it was found that the width of the electrochemical windows of both [C_4mim][BF_4] and [C_4mim][PF_6] were severely decreased when water (even very small amounts) was present. This phenomenon was attributed to water electrolysis occurring. Additionally, the presence of water had a strong influence on the diffusion rate of ionic and neutral species, leading the authors to suggest that a nanostructure consisting of polar and nonpolar regions is present in the ionic liquids. Such an inhomogeneity allows the neutral molecules to reside in less polar regions, whereas ionic species undergo fast diffusion in the more polar ("wet") regions (167).

The microscopic physical properties of mixtures of water with either [C_1mim]Cl or [C_1mim][PF_6] as functions of composition have been studied by molecular dynamics simulations. Although the two ionic liquids under investigation differ in their physical properties (the hexafluorophosphate exhibiting hydrophobic properties, while the chloride derivative is hydrophilic), little difference was found for their interaction with water. At low water concentrations, the water molecules are isolated from each other, and hydrogen-bond preferably to the respective anion rather than to other water molecules. Thus, at solutions with less than 50 mole% water, 35–40% of the water molecules are completely isolated from each other, and few large clusters of water exist. If water is in excess over the ionic liquid, a percolation network of water molecules is formed, with some isolated water molecules interacting with the anions and regions containing water clusters. These predictions from the modelling study are completely in accord with the conclusions from density studies (see Fig. 16). Such a continuous water network changes the mixture and its properties dramatically. For example, it was found that the molecular motion increases as the proportion of water increases. Some properties, such as the ion diffusion correlation times and the radical distribution functions, are independent of the hydrophobicity of the anion of the ionic liquid. On the other hand, the excess thermodynamic functions, the water diffusion coefficients and the reorientational correlation times are dependent on the nature of the anion (241).

For the example of [C_4mim][BF_4]-water mixtures, cation–cation, cation–anion and cation–water interactions were studied by NMR spectroscopy through intermolecular nuclear Overhauser enhancements (NOEs). It was found that a continuous increase in the water/ionic liquid ratio leads to a replacement of the hydrogen bonds between the ring hydrogen atoms and the fluorine atoms of the tetrafluoroborate with hydrogen bonds between the ring hydrogen atoms and the water molecules. This replacement does, however, not occur in an on/off switch fashion, but rather continuously; cation-anion interactions were still observable at a water/ionic liquid ratio of 1:1.8. The structural change leads to a breaking of the imidazolium-imidazolium cationic associations, thus increasing the distance between neighboring cations. Increasing amounts of water also gave rise to augmented interactions of the methyl moiety with the butyl moiety, indicating that an orientational change occurred, which allows the methyl moiety to be accommodated in closer vicinity to the butyl moiety. Also, conformational changes in the structure of the butyl chain with respect to the plane of the imidazolium ring were suggested. While the hydrogen bond formation between the cation and water molecules involves selectively the hydrogen atoms on the ring carbon atoms, a further increase in the water concentration renders the system less structured, with interactions also between the alkyl hydrogen atoms and water. Since the maximum water/ionic liquid mole ratio in this study was 1:0.9, no statement can be made to the structures in mixtures where water is in an excess over the ionic liquid (242).

Attenuated total reflectance and transmission infra-red spectroscopy was used in an extensive study of the molecular state of dissolved water in several ionic liquids based on the $[C_4mim]^+$ cation. Measurements were performed at concentrations of water up to the saturation point of water by absorption of moisture from the atmosphere (ie, concentrations where the ionic liquid is in molar excess over water). Welton and co-workers showed that at any water concentration up to the saturation point, water has distinct interactions *via* hydrogen bonding with the anions under study ($[PF_6]^-$, $[SbF_6]^-$, $[NTf_2]^-$, $[BF_4]^-$, $[ClO_4]^-$, and $[OTf]^-$), and areas of clusters or pools of water are not present. Instead, 2:1 complexes, in which both protons of water are bound to two discrete anions, $A^-\ldots H\text{-}O\text{-}H\ldots A^-$ (where A^- represents the anion of the ionic liquid) exist. An additional type of state of water was found with more nucleophilic anions (nitrate or trifluoroethanoate), and their ATR-IR spectra indicate the presence of clusters of water molecules in addition to the 2:1 complexes (103). The enthalpies of interaction of water with different anions were determined from the spectral shifts. They increase in the following order (103):

$$[PF_6]^- < [SbF_6]^- < [BF_4]^- < [NTf_2]^- < [ClO_4]^- < [OTf]^- < [NO_3]^-$$

From this study, no estimate as to the state of water at concentrations higher than the saturation point can be derived, and clusters or aggregates may be present in such a case. In fact, excess molar volume studies of $[C_4mim][BF_4]$–water mixtures have shown a sharp increase once water is present in excess over the ionic liquid mole fraction (32).

In order to study any potential interaction of the cations with water, the acidic hydrogen atoms (which would interact with the oxygen atom of the water) on the imidazolium ring were substituted by methyl moieties. No spectral evidence was found for the participation of the hydrogen atoms of the unsubstituted ring. However, since the affinity of the substituted homologues to water increased, the authors suggest that the strengths of hydrogen bonding with the anion must increase. Alternatively, more free volume is created by introducing methyl moieties into the ring, thus enabling water molecules to reach their preferred sites of binding more easily (103).

In conclusion, although there are, as yet, very few data available on the structure of pure ionic liquids or ionic liquid–cosolvent mixtures, it is obvious that it is influenced by several factors, which determine the physico-chemical properties. These factors are the size/nucleophilicity of the anion, the type of cation, the substituents (length and functionalities) on the cation, temperature, and the nature and concentration of additives, such as water or organic solutes.

11. Laboratory Applications

In recent years, ionic liquids have been used for a wide variety of applications (Fig. 19) (243), such as the recovery of biofuels (244) and the deep desulfurization of diesel oil (245) by extraction of butanol or sulfur-containing compounds, respectively, into the ionic liquid. Ionic liquids also have potential as lubricants (246), in solar cells (180,247,248), for heat storage (249), in nuclear fuel processing (90,136,225,250), in membrane technology (57,137,251–253), as sol-gel templates (254), and in the dissolution of cellulose (255).

Ionic liquids have also shown promise in some startling applications, such as embalming and tissue preservation. Pernak and co-workers found that 1-alkyoxy-3-methylimidazolium tetrafluoroborate did not cause tissue damage or changes to the tissue color. Furthermore, the microscopic morphology changed less than when the tissues were fixed in formalin (256).

[C_2mim][NTf_2] was studied as a propellant for colloid thrusters. These may become important for the positioning of small satellites or space missions, where accurate location of the spacecraft is required (257).

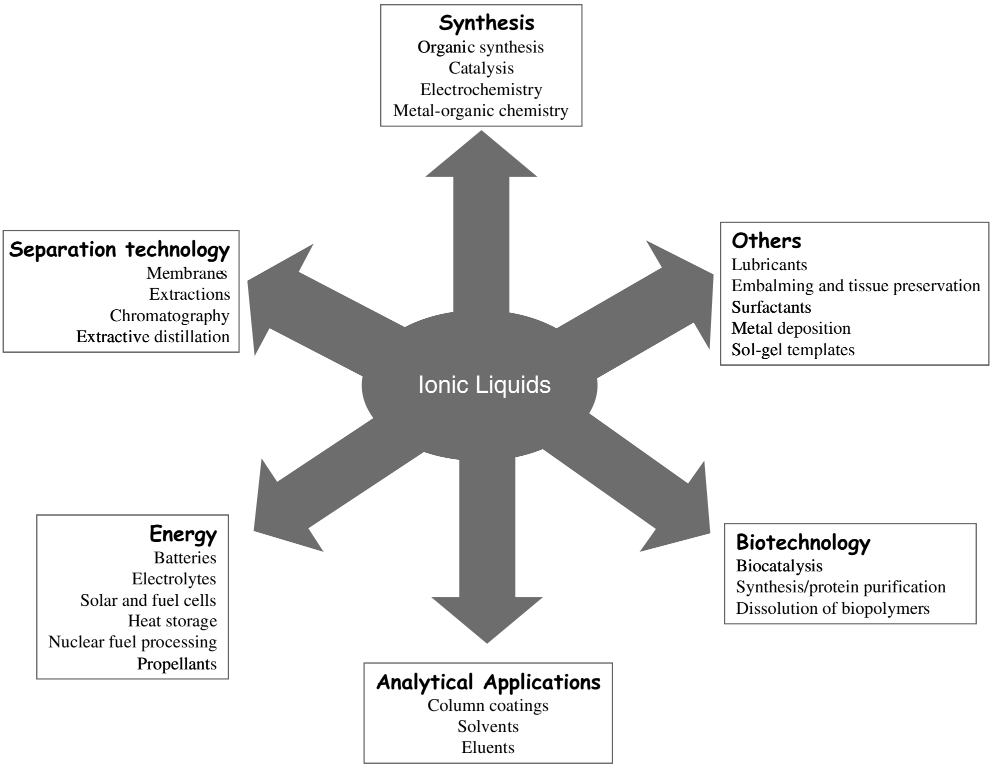


Fig. 19. Some Applications of ionic liquids.

Ionic liquid applications that have reached (or are close to) commercialization are discussed in Section 12.

11.1. Ionic Liquids as Solvents for Separations.

Ionic liquids can be combined with other fluids, such as water, supercritical fluids or fluorous phases, to give potentially benign systems for separation technology, eg, extraction or chromatography (258). The combination of their advantageous properties may offer new opportunities for the clean-up of existing chemical extraction processes, where they substitute for toxic, flammable and volatile organic solvents. In the following, interesting, and often unexpected, solvent-solute interactions are reviewed.

Liquid/Supercritical Fluid Extractions and Related Systems. Extraction from ionic liquids with a supercritical fluid is the ultimate method for “green” partitioning of phases, since commonly used volatile organic solvents as extracting media may cause harmful emissions. The first example of the combination of ionic liquids with supercritical fluids was reported by Brennecke and co-workers (212), who investigated the extraction of naphthalene from an ionic liquid. This study showed that extractions with ionic liquid−CO_2 systems are particularly suitable for substances that are hydrophilic or water-sensitive, and therefore do not permit aqueous extraction from ionic liquid media, or for poorly volatile or thermally labile products, for which distillation as a method of separation is not applicable (212).

Further studies showed that supercritical CO_2 can be used to quantitatively extract an array of organic solutes from $[C_4mim][PF_6]$. Substrates with high volatility and low polarity possess a higher solubility in supercritical CO_2, whereas such substrates with high polarity and aromaticity favor the ionic liquid phase. A correlation between the dipole moment and the amount of CO_2 necessary for the recovery was established (197).

Recently, various reports of catalytic reactions carried out in ionic liquids, from which the products are removed after the reaction using supercritical fluids, have been published (259–263). These publications illustrate that catalyst and ionic liquid recycling are feasible using this method.

Liquid/Liquid Extractions. Extraction of Organic Compounds. Rogers and co-workers (264) compared distribution ratios of uncharged and charged compounds in $[C_4mim][PF_6]$/water to octan-1-ol/water systems, octan-1-ol is often empirically used to obtain a hydrophobicity scale using radiochemical tracers, and found a close relationship between the two systems, the former being approximately one order of magnitude lower than the latter (Fig. 20). Charged, polar compounds have a lower partition coefficient than uncharged or non-polar substances, ie, they are better soluble in the ionic liquid (or octan-1-ol) than in water.

For acids (eg, benzoic acid) as well as for bases (eg, aniline), the partition coefficient can be controlled *via* alteration of the pH of the aqueous phase, as it is classically accomplished in separation science. Much like molecular solvents, ionic liquids tend to dissolve preferably nondissociated species (264). This behavior is somewhat against the rule-of-thumb and has not yet been explained: it would be expected that ionic species are more soluble in the ionic liquid than in molecular solvents. The same applies to more complicated molecules, such as the antibiotic erythromycin-A (265).

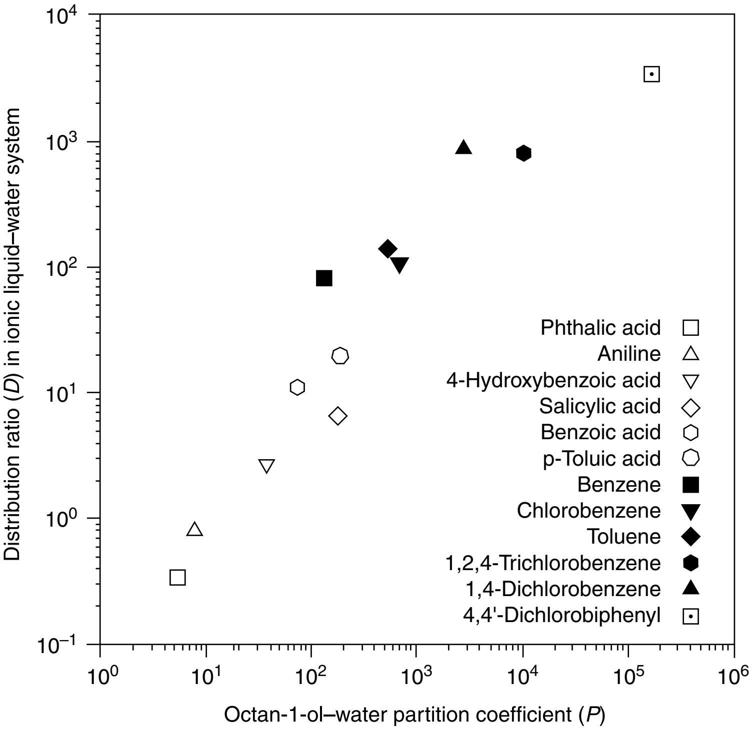


Fig. 20. Correlation of partitioning data between [C_4mim][PF_6]–water and octan-1-ol-water biphasic systems (264). Reprodued by permission of The Royal Society of Chemistry.

An environmentally benign alternative for the adjustment of the pH was demonstrated using recyclable gases, such as CO_2 and NH_3, on the example of the distribution of thymol blue between the ionic liquid phase and water (266). If the pH of the aqueous phase is low, eg, 1.5, thymol blue exists as the neutral zwitterion (red), which prefers the ionic liquid phase. Upon increasing the pH of the aqueous phase by addition of NaOH or NH_3, the yellow monoanion forms, which is distributed between both the aqueous and the ionic liquid phase. At very high pH, ie, above 10, a blue dianion forms, which prefers the aqueous phase (see Fig. 21). Bubbling CO_2 through this latter solution resulted in the reformation of the yellow species.

An additional advantage of ionic liquids in separation technology is the possibility of fine-tuning the solubility of a substrate by alteration of the alkyl chain length, eg, from butyl ([C_4mim][PF_6]) to octyl ([C_8mim][PF_6]). For example, thymol blue, which is distributed between the ionic liquid [C_4mim][PF_6] and the aqueous phase, enriches in the aqueous layer at pH 12 as mentioned above. However, if [C_8mim][PF_6] is used under the same conditions, the dye possesses a higher solubility in the ionic liquid phase than in water (266).

Although phase separation is generally fast, in some instances it can be further facilitated by choosing an ionic liquid with a melting point above room-temperature; in such a case, the extraction is carried out at elevated temperatures in a liquid-liquid system. Upon cooling, the ionic liquid solidifies together

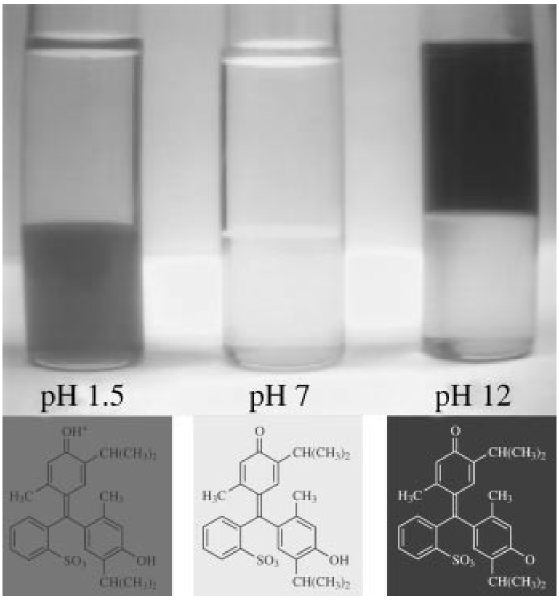
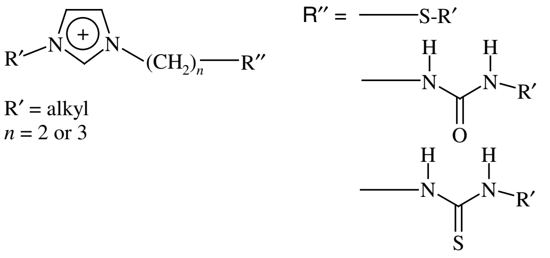


Fig. 21. Distribution of thymol blue between [C_4mim][PF_6] (lower phase) and water (upper phase) at different pH (266). Reproduced by permission of The Royal Society of Chemistry.

with the extracted substrate, which is easily isolated after decanting the aqueous phase (266).

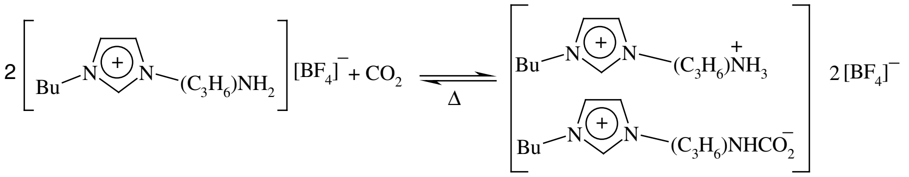
Extraction of Inorganic Compounds. Water-immiscible imidazolium-based ionic liquids have also been used to extract alkali and alkaline earth metals from aqueous media with the help of crown ethers (144,267–269). In summary, higher distribution coefficients were found for ionic liquids than for conventional organic solvents, due to the limited solubilities of ionic species in non-ionic organic solvents (267,269). In competitive metal extraction experiments, the anion of the metal salts does not exhibit an influence on their distribution. Such behavior is commonly observed in octan-1-ol extraction, whereas with chloroform, an anion effect of the metal salt is apparent. This finding was attributed to anion stabilization by hydrogen bonding (269). However, both the nature of the cation and anion of the ionic liquid play an important role. Thus, the distribution coefficient of the strontium(II) nitrate extraction is higher if the imidazolium cation is 2-methylated rather than possessing a proton in C-2 position, indicating that hydrogen bonding is an important factor. By alteration of the alkyl chain length of the cation, the solubility of the crown ether complex can be indirectly tuned, as it is dependent on the amount of water which co-dissolves in the respective ionic liquid (144,269). Additionally, if the ionic liquids contains the bis{(trifluoromethyl)sulfonyl}amide counterion, the extraction coefficients are higher than if the ionic liquid is based on hexafluorophosphate, indicating a key role of the anion in the solvation of the crown ether-Sr^{2+} complex (267).

Imidazolium-based hexafluorophosphate ionic liquids with thiourea, thioether or urea side chains have been designed for the extraction of mercury(II) and cadmium(II) from aqueous solutions (eq. 13) (73,270), allowing for enrichment of the metals in the ionic liquid independent of the pH of the aqueous phase. Additionally, doping the much cheaper [C_4mim][PF_6] with the thioether-derived ionic liquid often leads to comparable results as when using the thioether-based extractant in its pure form (73,270).



(13)

Gas/Liquid Extractions. Ionic liquids have been designed for the extraction of carbon dioxide from gas mixtures, eg, sour gas. By integrating a secondary amine into the alkyl chain on the imidazolium cation, it is possible to sequester carbon dioxide (see eq. 14) by formation of a carbamate. This reaction is reversible; the CO_2 may be driven off by heating under reduced pressure. The remaining ionic liquid can then be reused without loss of activity. The development of such application-specific materials demonstrates well that ionic liquids can be regarded as designer solvents (271).



(14)

Ionic Liquids in Chromatography. Due to their high thermal stability, ionic liquids with melting points close to 100°C have been investigated for application as stationary phases in gas chromatography (272). The ionic liquid combinations studied include tetraalkylammonium, 1-alkyl-3-methylimidazolium or 1-alkylpyridinium cations with anions such as benzoate, halides, hexafluorophosphate or tetrafluoroborate, immobilized on Chromosorb or silica (273,274). Generally, these ionic liquids behaved as nonpolar stationary phases towards nonpolar, Brønsted neutral analytes. However, they interact strongly with analytes containing proton-donating or -accepting groups, giving high retention. It was found that although [C_4mim]Cl and [C_4mim][PF_6] possess similar polarities, proton-donating or -accepting groups (eg, diols, alcohols, phenols, carboxylic acids, or amines) are retained to a higher extent in the chloride analogue, whereas for aliphatic and aromatic compounds, esters, aldehydes, ketones, and haloalkanes, the retention is higher in the [PF_6]$^-$ ionic liquid (274).

Activity coefficients at infinite dilution for alkenes, alkanes, alkylbenzenes and polar solutes have been determined by gas-liquid chromatography, using 1-butyl-4-methylpyridinium tetrafluoroborate, $[C_2mim][NTf_2]$ and $[C_2dmim][NTf_2]$ as stationary phases (275). It was found that intramolecular interactions between the solute and ionic liquid increase with the number of polarizable electrons in unsaturated substrates such as alkenes and aromatic compounds. This finding was assigned to more pronounced ion-induced dipole interactions. Both the $[C_2mim]^+$- and $[C_2dmim]^+$-based ionic liquids give similar values for the activity coefficients. Although ionic liquids based on either pyridinium or imidazolium cations follow similar trends, the former gave somewhat higher values (275).

Lower melting ionic liquids, in particular tetraalkylammonium nitrate and thiocyanate, can also be used as mobile phases. In cases where the viscosity or the melting point are too high, co-solvents, such as dichloromethane, water, ethanenitrile, methanol or tetrahydrofuran can be added to achieve suitable flow-properties (276). The decrease in viscosity of an ionic liquid, eg, of $[C_4mim][BF_4]$, upon addition of various organic solvents is illustrated in Figure 12 (32).

An interesting usage of ionic liquids in chromatography was presented by Novartis (277), who patented the use of ionic liquids as solvents in headspace gas chromatography. Unlike molecular solvents, chromatograms obtained using ionic liquids do not feature broad solvent peaks, limited temperature range and carry-overs from consecutive injections. Due to their negligibly low vapor pressure, interfering solvent peaks are not generated, lower detection limits achieved, and the application range of headspace gas chromatography extended (277).

11.2. Electrochemical Applications. *Batteries.* Ionic liquids have been investigated for application as electrolytes. In fact, the development of electrolytes with low melting point such as 1-ethylpyridinium bromide/aluminium(III) chloride (36), and subsequently, the air- and moisture stable second-generation salts (38), triggered interest in the investigation of these media for other purposes, such as solvents in synthesis and extraction technology. Their high conductivities (Section 8.3), large electrochemical windows (Section 8.4), and wide liquid ranges (Section 8.1) are ideally suited for the use as electrolytes in batteries. For example, the application of pyridinium- and imidazolium-derived ionic liquids in conjunction with inexpensive graphite electrodes has advantages over the conventional “rocking-chair” battery, which is complex in its synthesis, purification, and assemblage (278). This is mainly due to the use of cathodes made from transition metal oxides, and electrolytes made from lithium salts dissolved in organic carbonates and ethers. Both components require rigorous purification. In batteries based on ionic liquids, on the other hand, only one component needs purification, no organic solvent is required, and the toxicity of the components employed is relatively low. Additionally, the battery can be assembled in the discharged state (278), and is unlikely to be a fire hazard!

Although many electrolytes developed for battery use are based on haloaluminate molten salts, some newer developments have shown that the second-generation ionic liquids, such as $[C_2mim][NTf_2]$, have excellent properties for this purpose as well (70). For example, ionic liquids, in particular those based on fluorinated anions such as $[NTf_2]^-$, have been investigated as replacements for organic carbonate electrolytes in lithium ion batteries. Due to their ionic nature, ionic liquids can act as both the electrolyte and the source of the intercalative guest species ("dual intercalating molten electrolyte") with graphite electrodes. Especially, ionic liquids based on the C-2-substituted 1,2,3-trialkylimidazolium cations showed sufficient stability during multiple charge-discharge cycles (278,279).

The interested reader is further referred to a first-hand review by Wilkes (280).

Dye-sensitized Solar Cells. Dye-sensitized solar cells (281) are used to directly generate electricity from light. A dye absorbs light and releases electrons which are collected at a counter electrode. The dye is regenerated by electrons from an electrolyte containing a redox couple. Due to their negligibly low vapor pressure, ionic liquids featuring thermal and electrochemical stability, high conductivity, and low viscosity have been used as both redox couples and electrolytes. Grätzel and co-workers have initiated research in this area, and shown that ionic liquids based on the bis{(trifluoromethyl)sulfonyl}amide or trifluoroethanoate anions can serve as electrolytes (70,180,247,282), while ionic liquids based on iodide, such as the [C_3mim]I, are employed to generate the $[I_3]^-/I^-$ redox couple while simultaneously acting as electrolytes (283).

Electrosynthesis. Conducting polymers such as polypyrrole and polythiophene (106,284–286) or poly(paraphenylene) (22,287,288) can be made by electrochemical oxidative dehydrogenation. These polymers, which are conductive for both, ions and electrons, find application in display devices, mechanical actuators or in corrosion prevention (284,289,290). Although some polymers can be synthesized in aqueous or organic solution, others require concentrated sulfuric acid or liquid sulfur dioxide. These can be substituted with ionic liquids due to their negligibly low vapor pressure, wide electrochemical window, electrochemical stability and sufficient conductivity. Thus, poly(3,4-ethenedioxythiophene), polypyrrole and polyphenylene were synthesized in 1,3-dialkyl- imidazolium tetrafluoroborates, hexafluorophosphates, bis{(trifluoromethyl)sulfonyl}amides or tris (pentafluoroethyl)trifluorophosphates (286,290,291), often with improved properties of the polymers obtained.

Electrodeposition of Metals. Electrodeposition is an important tool in the purification of metals, manufacture of nanocrystalline metals and nanoscale semiconductors, and is the historic origin of ionic liquids (36). A wide electrochemical window (see Section 8.4) is a prerequisite for the effective deposition of highly electropositive elements such as aluminium, silicon or lithium (55,158,292), transition metals (293), and alloys (294,295). Ionic liquids show advantages over aqueous solutions: deposits with superior mechanical properties are obtained, and the risk of dihydrogen evolution, as it is frequently observed in aqueous solution, is avoided (294,296).

11.3. Transition Metal-catalyzed Reactions in Ionic Liquids. Many organic syntheses incorporating ionic liquids have been reported in the literature. They can be categorized into reactions that occur without the interaction of an added catalyst, and those in which a transition metal facilitates the reaction. The benzoin condensation (50) and nitration (297) are examples where the ionic liquid solvent also acts as the catalyst. Here, only those reactions involving metal catalysis (mainly transition metals) are discussed, since, in these instances, interesting effects such as higher catalytic stability, improved recycling or selectivity are frequently observed, in addition to replacing volatile organic solvents. Conclusions are drawn from the literature with respect to particular features of transition metal catalysis in ionic liquids and ecological improvements achieved. Noncatalytic reactions have not been included here, as they have been reviewed in detail elsewhere (4,27–30,163,298,299).

The obvious advantage of using ionic liquids instead of volatile organic solvents in metal-catalysed reactions is the immobilization of the catalyst in the ionic liquid phase, thus allowing for facile catalyst recycling after the removal of the products. The term "immobilization" is used in this context to indicate the strong affinity of the catalyst to the ionic liquid phase. Exploiting this concept, a wide variety of transition metal-catalysed reactions has been reported. However, since the chemical and physical properties (*vide supra*) of ionic liquids are considerably different to those of molecular solvents, this is, in most cases, not just achieved by simple substitution of solvent. Instead, the catalyst complexes usually used in organic solvents may need to be adapted to the ionic medium, eg, by choosing ionic ligands to avoid leaching. Due to this alteration of the ionic environment, the reaction mechanism might proceed through different intermediates. Additionally, some ionic liquids may form carbenes and thus act as a catalyst ligand. In the following sections, transition metal-catalysed reactions carried out in ionic liquids are discussed, with respect to the above issues.

Hydrogenation. *Hydrogenation of Mono-unsaturated Olefins.* Chauvin and co-workers demonstrated the hydrogenation of pent-1-ene carried out in $[C_4mim][SbF_6]$ using H_2 and $[Rh(nbd)(PPh_3)_2][PF_6]$ (where nbd = bicyclo[2.2.1] hepta-2,5-diene) as the catalyst precursor. The complex is soluble in the ionic liquid, whereas the solubility of the substrate and product is very low (19).

The reaction using an ionic liquid leads to a five-fold increase in turnover frequency over that when carried out in propanone. This finding is attributed to the non-coordinating character of the $[SbF_6]^-$ anion, which, unlike propanone, does not interact with the rhodium catalyst. On the other hand, when ionic liquids with strongly coordinating anions, such as chloride, are used in the hydrogenation experiments, the rate of hydrogenation drops while the selectivity to the isomerization product pent-2-ene increases. The ionic liquid clearly plays not only the part of the solvent, but the choice of anion determines whether hydrogenation or isomerisation takes place (19).

In a similar fashion, the reactivity of the precursors $[RhCl(PPh_3)_3]$ and $[RuCl_2(PPh_3)_3]$ was investigated in the hydrogenation of cyclohexene (300), hex-1-ene and cyclohexene (116) with H_2 in $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ (300). In the latter instance, no undesired isomerization products are observed.

An interesting approach was chosen by Dupont and co-workers (301). The authors investigated iridium nanoparticle-formation in $[C_4mim][PF_6]$ by ligand reduction and displacement of $[IrCl(cod)]_2$ (where cod = 1,5-cyclooctadiene) with H_2. The particles formed are highly active in the hydrogenation of dec-1-ene and other alkenes and a higher catalytic activity is achieved than by classical transition metal catalyst precursors in ionic liquids under similar reaction conditions. Product separation is easily achieved by phase-separation, and the ionic liquid containing the dispersed particles can be recycled for five times without any loss in catalytic activity. A further advantage is the facile separation of the catalyst particles by centrifuging or filtration from the ionic liquid, should this be necessary (301). However, some of the conclusions of this work have been questioned, and it is suggested that carbenes formed *in situ* stabilize the nanoparticles, and not the ionic liquid *per se* (302).

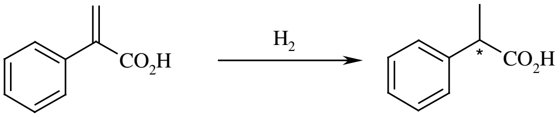
Recently, Tumas and co-workers demonstrated that supercritical CO_2 can be used to remove the products from the catalyst-containing ionic liquid phase (259). On the example of the hydrogenation of dec-1-ene and cyclohexene using $[RhCl(PPh_3)_3]$ in $[C_4mim][PF_6]$, it was shown that efficient catalyst recycling is feasible.

Selective Hydrogenation of Dienes. The selective hydrogenation of dienes, such as cyclohexa-1,3-diene and 2-methylbuta-1,3-diene with H_2 in the presence of rhodium(I) was achieved in $[C_4mim][SbF_6]$. Cyclohexa-1,3-diene yields selectively (selectivity 98%, conversion 96%, turn-over frequency 3.2 min^{-1}) cyclohexene, whereas 2-methylbuta-1,3-diene gives a mixture of 2-methylbut-1-ene, 3-methylbut-1-ene and 2-methylbut-2-ene. These results are comparable to those obtained in organic solvents (115). The selective hydrogenation of buta-1,3-diene to but-1-ene using either $[RuCl_2(PPh_3)_3]$ or $K_3[Co(CN)_5]$ in $[C_4mim][BF_4]$ was also studied (116). The ruthenium-based catalyst precursor unselectively yields a mixture of but-1-ene, *cis*- and *trans*-but-2-enes and butane, whereas the cobalt-based precursor gives selectively but-1-ene at 25°C. At higher temperatures, however, the selectivity decreases and *trans*-but-2-ene is produced as well.

$[Pd(acac)_2]$ (where Hacac = pentane-2,4-dione) was used in $[C_4mim][BF_4]$ as a catalyst precursor in the selective hydrogenation of buta-1,3-diene to butenes at 50°C under several bar of H_2. The product forms a second phase that is easily decanted, and the catalyst-containing ionic liquid phase can be reused. However, if unsaturated acids are hydrogenated, eg, hexa-2,4-dienoic acid, the formation of metallic palladium is observed, and some palladium is extracted into the product phase (298).

Hydrogenation of Arenes. The hydrogenation of arenes, such as benzene, toluene and cumene, with H_2 to cycloalkanes was investigated in $[C_4mim][BF_4]$ using the cluster $[H_4Ru_4(\{\eta\}^6\text{-}C_6H_6)][BF_4]_2$ as a catalyst precursor. The hydrogenation is carried out in a liquid–liquid biphasic system at 60 bar of H_2 and 90°C. The turnover frequencies are similar to those observed in the hydrogenation using the same catalyst under aqueous-organic biphasic conditions. The advantage of using ionic liquids in this case is that the exhaustive work-up to remove traces of organic substances and catalyst from the aqueous phase is avoided. The ionic liquid, by contrast, is extracted to remove traces of organics, and may be reused (118,120).

Asymmetric Hydrogenation. The asymmetric hydrogenation of 2-phenylacrylic acid by H_2 was investigated in a mixture of $[C_4mim][BF_4]$ and isopropanol (3/35 v/v) using $[Ru\{(S)\text{-binap}\}(O_2CCH_3)_2]$ as catalyst precursor (eq. 15). The authors (117) did not report whether this reaction proceeds without the addition of the organic solvent.



(15)

Isopropanol is used to obtain a biphasic reaction mixture, in which the catalyst is immobilized in the ionic liquid phase and the product is simultaneously extracted into the lighter organic phase. Enantiomeric excesses of up to 84% of the *S* enantiomer of 2-phenylpropanoic acid are obtained, which is comparable to the reaction outcome in methanol, but with the advantage of easier product separation and catalyst recycling (117).

The effect of H_2 pressure on the rhodium-catalyzed asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid using (−)-1,2-bis((2*R*,5*R*)-2,5-diethylphospholano)benzene (cyclooctadiene)rhodium(I) trifluoromethylsulfonate dissolved in a biphasic mixture of either $[C_4mim][BF_4]$ or $[C_4mim][PF_6]$ with propan-2-ol was studied. Both the conversion and the enantiomeric excess increase with increasing dihydrogen solubility, and are therefore better in $[C_4mim][BF_4]$ than in $[C_4mim][PF_6]$ (see Section 8.10). The authors report that the ionic liquid catalyst phase can be recycled four times, after which a significant drop in conversion is observed due to catalyst leaching into the organic phase (208). The use of the dimethyl analogue of the above catalyst precursor in the hydrogenation of methyl α-acetamidoacrylate and methyl α-acetamidocinnamate in a $[C_4mim][PF_6]$—propan-2-ol biphasic mixture was also studied by Guernik *et al.* (303). The conversions and enantiomeric excesses of both substrates are similar to runs performed in a propan-2-ol monophasic system, and recycling is possible for five cycles, although the conversion somewhat decreases after the first cycle. Most importantly, this study shows that the air-sensitive catalyst precursor is stabilized against oxidation when dissolved in the ionic liquid; exposure to air for 24 h did not lead to a decrease in conversion or enantiomeric excess in a subsequent run (303).

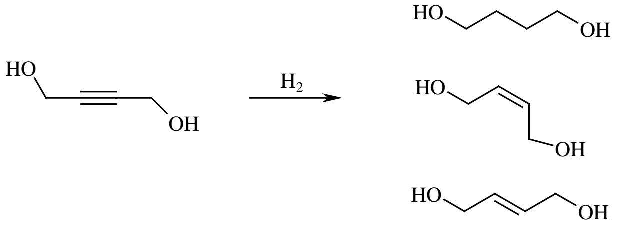
Recently, ionic liquids have been combined with supercritical fluids in the asymmetric hydrogenation of tiglic acid to 2-methylbutanoic acid, catalysed by $[Ru\{(R)\text{-tolylbinap}\}(O_2CCH_3)_2]$. The reaction proceeds with high enantioselectivity and conversion, and the product is separated using supercritical CO_2. Recycling of the ionic liquid-catalyst phase is possible without significant loss of conversion or selectivity (304).

Instead of using H_2, Andersen and co-workers achieved enantioselective hydrogenation by H_2 transfer from propan-2-ol to acetophenone, yielding a 92% ee of 1-phenylethanol. The catalytic system used consisted of $Rh(O_2CCH_3)_3$/(−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (2/3) in the ionic liquid ethyltrioctylphosphonium 4-toluenesulfonate. This ionic liquid is solid at room-temperature but liquid at reaction temperature (120°C), and therefore the product phase can be easily decanted after the reaction mixture has cooled to room temperature (305).

Other Hydrogenations. Tumas and co-workers reported the hydrogenation of carbon dioxide in the presence of dialkylamines to produce *N,N*-dialkylformamides, using $[RuCl_2(dppe)_2]$ (where dppe = 1,2-bis(diphenylphosphino)ethane) as catalyst precursor. The products of such a reaction are highly soluble in ionic liquids, leading to a low recovery rate when using supercritical CO_2. However, after saturation of the ionic liquid phase with product, quantitative recovery became feasible (259).

The hydrogenation of but-2-yne-1,4-diol (eq. 16) was investigated using the hydrophobic $[Rh(\{\eta\}^4\text{-}C_7H_8)(PPh_3)_2][BF_4]$ and H_2 in a water-$[C_8mim][BF_4]$

mixture in an “optimal” reaction mode (193). Under the reaction conditions (80°C, 60 bar), a monophasic homogeneous reaction mixture is present, but the product-containing aqueous phase separates from the catalyst-containing ionic liquid phase at room temperature. The products but-2-ene-1,4-diol and butane-1,4-diol are preferentially water-soluble at room temperature, and can thus be easily decanted from the catalyst phase, which is reused in four subsequent runs. Unfortunately, a slow decomposition of the catalyst is observed (193).

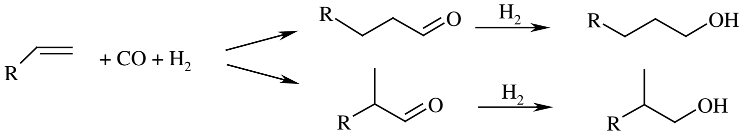


(16)

Gas Phase Hydrogenation Over Gels. The preparation of a free-standing, flexible, catalytically-active membrane composed of a poly(vinylidene fluoride)-hexafluoropropylene copolymer and an air-stable ionic liquid consisting of a perfluorinated anion (eg, $[BF_4]^-$, $[OTf]^-$ or $[PF_6]^-$) and the 1,3-dialkylimidazolium cation (eg, $[C_2mim]^+$) has been described (251,253). The membranes are rubbery films, transparent or slightly translucent, and possess high ionic conductivities. Such membranes were tested for the hydrogenation of propene (251,253) and ethene (253) with H_2. A mixture of alkene and H_2 is placed in contact with the membrane. The hydrogenation takes place during diffusion, and the alkane is collected on the other side of the membrane. For this application, either palladium on charcoal (251) or $[Rh(nbd)(PPh_3)_2]$ (where nbd = bicyclo[2.2.1]hepta-2,5-diene) (253) were dispersed into the films as heterogeneous catalysts. The activity of the catalyst remains constant throughout the experiment. The fact that both the polymer and the ionic liquid are nonvolatile and thermally stable allows the gels to be operated at elevated temperatures.

Hydroformylation and Carbonylation and Related Reactions. The first report, by Parshall, on hydroformylation, using an ionic liquid as solvent, appeared in 1972 (306). He studied the platinum-catalyzed hydroformylation of ethene in $[Et_4N][SnCl_3]$ (40,306,307). Knifton extended this investigation to platinum(II) and palladium(II) halide catalyst precursors bearing phosphine ligands for the hydroformylation of propene, and ruthenium catalysts for the conversion of octene and other alkenes (42,308,309). Shortly after the discovery of second-generation imidazolium-based ionic liquids (38), interest in hydroformylation was revived, and is one of the most investigated catalytic reactions using ionic liquids to date.

Thus, the hydroformylation of pent-1-ene was studied (see eq. 17) using the neutral $[Rh(CO)_2(acac)]/PPh_3$ catalyst precursor (where Hacac = pentane-2,4-dione) in $[C_4mim][PF_6]$ and $[C_2mim][BF_4]$ (115). The hexanal products are poorly soluble in these ionic liquids, and, thus, form a second phase that can be simply recovered by decantation. However, the rhodium catalyst leaches in small quantities into the organic phase. This can be avoided when polar ligands, such as the monosulfonated and trisulfonated triphenylphosphines are employed, since their affinity to the ionic liquid phase is higher than to the hexanal phase. However, the use of these ionic ligands gives lower yields than PPh_3, and the process thus requires further optimization (19,310).



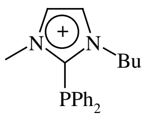
(17)

The hydroformylation of hex-1-ene to heptanal, 2-methylhexanal and 2-ethylpentanal catalyzed by $[Rh_2(O_2CCH_3)_4]$ was carried out in various phosphonium 4-toluenesulfonates (311). Good conversions were obtained, and the product distribution of the unbranched to branched isomers is strongly dependent on the ionic liquid. However, ionic liquids containing very bulky phosphonium cations, such as butyl- and octyltriphenylphosphonium 4-toluenesulfonate, are not stable towards hydroformylation. The alkyl groups are eliminated from the phosphorus to give the corresponding alkene (butene and octene), which is successively hydroformylated (311). However, this is one of the worst papers ever to be published in the field of ionic liquids, and its contents should be treated with high scepticism.

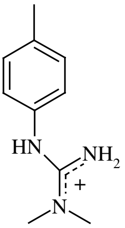
Methylpent-3-enoate was selectively hydroformylated to yield methyl-6-oxo-hexanoate in $[C_4mim][PF_6]$, using $[Rh(acac)(CO)_2]$ as catalyst precursor (where Hacac = pentane-2,4-dione). Keim and co-workers found that by addition of phosphine ligands, such as 2,2′-bis{([2,2′-bis{4-methoxy-6-*t*-butyl}phenoxy] phosphino)-oxyl}-1,1′-binaphthyl, the regioselectivity can be controlled, and thus, up to 47% of methyl-6-oxo-hexanoate is obtained, similar to when the reaction is carried out in toluene. However, the turnover frequency is doubled in ionic liquids. Furthermore, the catalyst is reusable when used in $[C_4mim][PF_6]$, whereas catalyst activity is quickly lost in dichloromethane or toluene (312).

Recent investigations have focused on the immobilization of the catalyst in the ionic liquid phase, and several patents are concerned with this issue (313,314). Using the example of oct-1-ene, Wasserscheid and co-workers (196) showed that a ratio of unbranched to branched isomer of 16.2/1 is obtained with a selectivity to the nonanal of 94%, by using 1,1′-bis(diphenylphosphino)cobaltocenium hexafluorophosphate as ligand on the $[Rh(CO)_2(acac)]$ catalyst precursor (where Hacac = pentane-2,4-dione). The reaction is carried out in liquid–liquid biphasic mode, which allows for easy solvent and catalyst reuse after the reaction is complete. The affinity of the catalyst for the ionic liquid phase is very high; the rhodium leaching into the organic layer is less than 0.2%. Similar results were obtained by using either a cationic guanidinium-modified diphosphine ligand in the rhodium-catalysed hydroformylation of octene in $[C_4mim][PF_6]$ (315), or the monosubstituted cationic guanidinium triphenylphosphine ligand in the hydroformylation of hexene in $[C_4mim][BF_4]$ (198). Both ligands retained the rhodium catalyst quantitatively in the ionic liquid phase; the rhodium content in the organic phase was under the detection limit of ICP analysis. The huge advantage of this approach, ie, catalyst-immobilization by coordination to a cationic phosphine ligand, lies in the fact that the reaction rate is as high as when using neutral phosphine ligands. Anionic phosphine ligands, on the other hand, lead to a reduced reaction rate (*vide supra*); this disadvantage may, however, be overcome when using a continuous flow process operating with supercritical CO_2 as the mobile phase (leaching <1 ppm) (260).

Sirieix *et al.* successively designed a cationic phosphine ligand which resembles a typical ionic liquid cation (**1**) (316). Olivier-Bourbigou and co-workers (**2**) (198), and Wasserscheid and co-workers (**3**) and (**4**) (317,318) used similar ligands and applied this concept to hydroformylation reactions.



(**1**)



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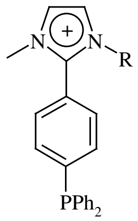

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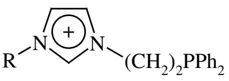
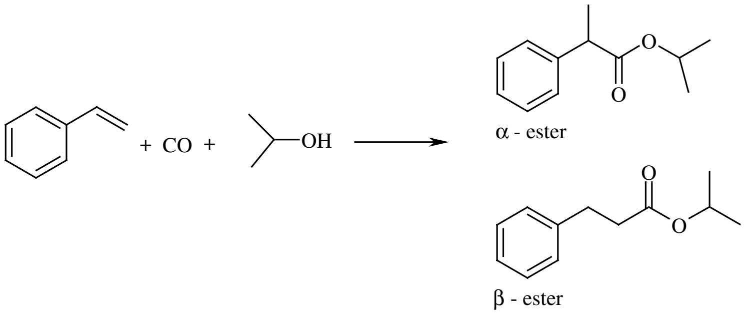


(**4**)

Dupont and co-workers demonstrated that styrene derivatives undergo hydroesterification by carbon monoxide and isopropanol in a liquid–liquid biphasic system, consisting of $[C_4mim][BF_4]$ and cyclohexane (319). The catalyst precursor (which is derived from $[PdCl_2(PhCN)_2]$, (+)-neomenthyldiphenylphosphine and 4-toluenesulfonic acid) is soluble in the ionic liquid phase, whereas isopropanol dissolves in the upper cyclohexane layer. By this method, styrene gives good yields of isopropyl 1-phenylpropanoate with very high selectivity (see eq. 18) (319). This ester is a valuable product since it is used as precursor in nonsteroidal antiinflammatory agents. Although similar results are obtained in the absence of the ionic liquid, ie, in a homogeneous system, this protocol provides a means of easy catalyst separation from the product phase, although further optimization for reducing the catalyst leaching has to be carried out (319).



(18)

The carbonylation of various bromobenzenes with an alcohol in the presence of triethylamine was studied using $Pd(acac)_2/PPh_3$ (where Hacac = pentane-2,4-dione). The conversions achieved in either $[C_4mim][BF_4]$ or $[C_4mim][PF_6]$ are higher than when the reaction is carried out in an excess of the reactant alcohol. However, upon recycling of the ionic liquid/catalyst mixture, the yields drop due to leaching of the triphenylphosphine, and palladium black precipitation (320). In a more extensive study, the carbonylation of various haloarenes in the presence of a nucleophile and a base was investigated using a diiodobis(benzothiazolylidene)-

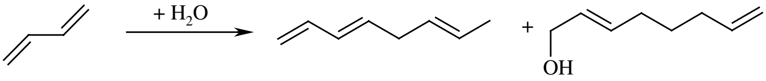
palladium(II) precursor. When using ionic liquids as solvents, higher pressures are necessary than in conventional solvents, which can be explained by the lower solubility of CO in ionic liquids (see Section 8.10). Furthermore, the reaction proceeds best in ionic liquids consisting of coordinating anions and tetraalkylammonium cations. The recycling of the catalyst and ionic liquid is quantitative. However, the accumulation of the by-product triethylammonium halide in the ionic liquid leads to an increase in viscosity, which inhibits further reuse after the fifth cycle (321).

Silylformylation of oct-1-yne was carried out in the presence of a rhodium catalyst, dimethylphenylsilane and CO in [C_4mim][PF_6] to yield 3-(dimethylphenylsilyl)-2-hexylpropenal in the pure *Z*-configuration. Recycling is possible, giving a total turn-over number of 290. Unfortunately the selectivity decreases when other alkynes, such as phenylethyne, are used (322).

The results obtained in the alternating copolymerization of styrene and carbon monoxide, which is formally also a carbonylation reaction, have been summarized (*vide infra*).

Dimerization, Hydrodimerization, Oligomerization and Polymerization. Much research on the areas of dimerization, oligomerization (14,20,323) and polymerization (21,288) has been carried out in the first-generation ionic liquids. For example, the nickel-catalyzed dimerization reactions of lower olefins were extensively studied by the groups of Chauvin (15–17,19,20,115,324), Dupont (14) and Wasserscheid (18). The research efforts of Chauvin's group lead to the development of the Difasol process (and a Nobel Prize), which has been licensed by IFP (see Section 12).

Dupont and co-workers (186,325) investigated the dimerization and hydrodimerization of buta-1,3-diene to octa-1,3,6-triene and octa-2,7-dien-1-ol in second-generation ionic liquids such as [C_4mim][BF_4] (see eq. 19).

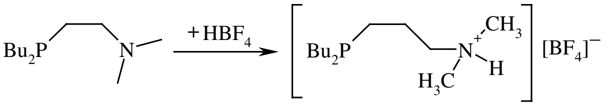


(19)

Different palladium(II)-ligand systems were tested, but simple palladium(II) ethanoate gives similar results with respect to selectivity and conversion, so that at conversions of 30%, 10–20% of the dimer and 80–90% of the hydrodimer are formed. This led to the suggestion that an imidazole-2-ylidene complex (see Section 7.2) may be formed *in situ* by all catalytic systems used. The dimer and hydrodimer are both soluble in [C_4mim][BF_4] at room-temperature, but phase-separation occurs upon cooling to 5°C. This facilitates catalyst recycling and thus the ionic liquid–catalyst solution can be reused for several runs without significant loss of catalytic efficiency (186).

The selective cyclodimerization of 1,3-butadiene to 4-vinylcyclohexene by a catalyst prepared by reduction of [{$Fe(NO)_2Cl$}$_2$] using zinc in [C_4mim][BF_4] was described by Dupont and co-workers (326). This biphasic reaction allows for simple catalyst recycling by decanting off the lighter product phase. The system is more selective than under homogeneous conditions, ie, when toluene acts as the solvent, and turn-over frequencies are also higher. Additionally, recycling is feasible for three times without any loss of catalytic activity or selectivity (326).

Methyl acrylate was dimerized to the industrially interesting Δ^2-dihydrodimethylmuconate in a $[C_4mim][BF_4]$-toluene biphasic continuous mode in the presence of $Pd(acac)_2$ as precursor (where Hacac = pentane-2,4-dione) and a cationic phosphine ligand (eq. 20) (327). This system is advantageous, because the presence of the weakly coordinating tetrafluoroborate anion increases the reaction rate, as expected from previous studies in absence of ionic liquids. Secondly, unlike tributylphosphine, the cationic ligand is almost quantitatively retained in the ionic liquid–catalyst solution, thus allowing an overall turn-over number of more than 4000, with a selectivity of >90% (327).



(20)

In 2001, the oligomerization of ethene to higher α-olefins was investigated in second-generation, water-stable ionic liquids in biphasic mode using a cationic nickel catalyst. It was found that traces of water and chloride decrease the activity of the catalyst in $[C_4mim][PF_6]$. Catalyst leaching into the organic phase is <0.1%, linear alk-1-ene selectivity high, and a turn-over frequency of over 12,000 h^{-1} is achieved, although it decreases somewhat upon recycling of the catalyst-containing ionic liquid layer (177). The authors proposed that the combination of high polarity (questionable!) and the low coordination ability of the ionic liquid is responsible for the high activity of the catalyst, which is higher than in butane-1,4-diol or dichloromethane. If longer alkyl chain analogues of the ionic liquid are used, the solubilities of the products increase, which ultimately leads to a decrease in catalytic activity. Higher solubility also leads to an increase of the Schultz-Flory distribution (177).

Second-generation ionic liquids have also been investigated in polymerization reactions (328). Haddleton and co-workers demonstrated that methyl methacrylate can be polymerized in a *monophasic* living radical reaction mediated by copper(I)–*N*-propyl-2-pyridylmethanimine in $[C_4mim][PF_6]$. The reaction rates are as fast as in conventional polar/coordinating solvents, yielding products of relatively low polydispersity and molecular mass. The polymer is removed from the ionic liquid phase by extraction with toluene, and the recycling of the ionic liquid and catalyst is feasible (122,329).

Similarly, $[C_4mim][PF_6]$ can be used for the biphasic atom-transfer radical polymerization, if a monomer with longer alkyl chain, as in butyl, hexyl or dodecyl acrylate, is used. In these cases, the monomer forms a second phase due to its low solubility in the ionic liquid, where the catalyst CuBr is almost selectively dissolved and the initiator ethyl 2-bromopropanoate is present in both ionic liquid and monomer phase. This system leads to almost quantitative conversions at room temperature, and the product phase contains <0.1% of the catalyst. The extent of side-reactions (such as disproportionation), leading to bromide-free saturated and unsaturated end groups, is less pronounced in the presence of ionic liquids than when performed in the absence of solvent (330).

Phenylethyne was polymerized by various rhodium(I) complexes in the presence of triethylamine as co-catalyst in $[C_4mim][BF_4]$ or $[C_4py][BF_4]$. The catalytic activity of [Rh(nbd)(acac)] (where nbd = bicyclo[2.2.1]hepta-2,5-diene and Hacac = pentane-2,4-dione) is essentially the same in either of the above ionic liquids, but the molecular weights of the polymers obtained vary considerably: in the former ionic liquid, a molecular weight of around 200,000 is obtained, whereas in the latter case, the molecular weight is only 100,000 under identical reaction conditions. The reaction is very fast: it proceeds to completion within minutes, with extremely high *cis* selectivity (331).

The effect of the nature of the ionic liquid solvent and other reaction parameters on the alternating co-polymerization of styrene and carbon dioxide, using $[Pd(bipy)_2][PF_6]_2$ (where bipy = 2,2′-bipyridine) as catalyst precursor, was investigated in detail. The yield, turn-over number, and polydispersity of the product can be adjusted by the choice of ionic liquid, and hydrophobic ionic liquids perform better than hydrophilic ones. Thus, the yield increases in the order of $[BF_4]^- < [PF_6]^- < [NTf_2]^-$ for a given cation, and with increasing alkyl length from $[C_4py]^+$ to $[C_8py]^+$. However, longer alkyl substituents on the cation also lead to higher leaching of palladium metal into the polymer. Ionic liquids with lower viscosity give higher yields due to increased CO diffusion from the gaseous phase into the ionic liquid. Under optimized conditions, a polyketone productivity of 24 kg polymer per g palladium with a polydispersity of 1.7 is achieved. This protocol gives higher yields, turn-over frequencies and polydispersities than in conventional molecular solvents, suggesting that different reaction mechanisms operate in these solvents. Recycling of the catalyst and ionic liquid is feasible for four cycles without significant loss of activity (182).

Conversely, Rogers and co-workers reported that under similar conditions, only polystyrene is formed in pure $[C_6py][NTf_2]$, but addition of methanol suppresses its formation, and the copolymer is formed selectively. Both the ratio of ionic liquid to methanol, and of solvent to reactants, influence the yield and polydispersity, and under optimized conditions, a polyketone productivity of 2.7 kg per g palladium was achieved (126).

Metathesis. The first metathetic reaction carried out in ionic liquids was reported in 1995 by Chauvin and co-workers (19). These authors used $W(OAr)_2Cl_4$ complexes (where ArOH = 2,6-diphenylphenol or 2,4,6-triphenylphenol) dissolved in Lewis acidic 1-butyl-3-methylimidazolium chloride–$AlCl_3$–$EtAlCl_2$ ionic liquids. Either pent-1-ene or a mixture of cyclopentene and pent-2-ene was used as a substrate. The active species are soluble in the ionic liquid and remain there during the work-up procedure (decantation of the hydrocarbon layer), so that they can be reused several times (19). Tungsten(VI) chloride and sodium perrhenate(VII) were also investigated as catalyst precursors. Interestingly, fast isomerization to hex-2-ene occurs, so that the main product is oct-4-ene. Both catalyst systems give only low yields at high catalyst concentrations of 10%, which increases by addition of tetrabutyltin(IV) (332).

The ring-closing metathesis or polymerization of α-ω-dienes in neutral first-generation, or second-generation, ionic liquids catalyzed by the catalyst types presented in Fig. 22 was patented by Bayer in 2000 (333).

Grubbs first- and second-generation catalyst precursors (see Fig. 22) have been used for the ring-closing metathesis of 1,5-diallyl-3-benzyl-5-isobutylimidazolidine-2,4-dione, and other substrates (334).

$[C_4mim][PF_6]$ was tested for the ability to retain the ruthenium catalyst in the ionic liquid phase. Although some leaching occurs with the first-generation catalyst precursor, this is substantially reduced with the second-generation catalyst

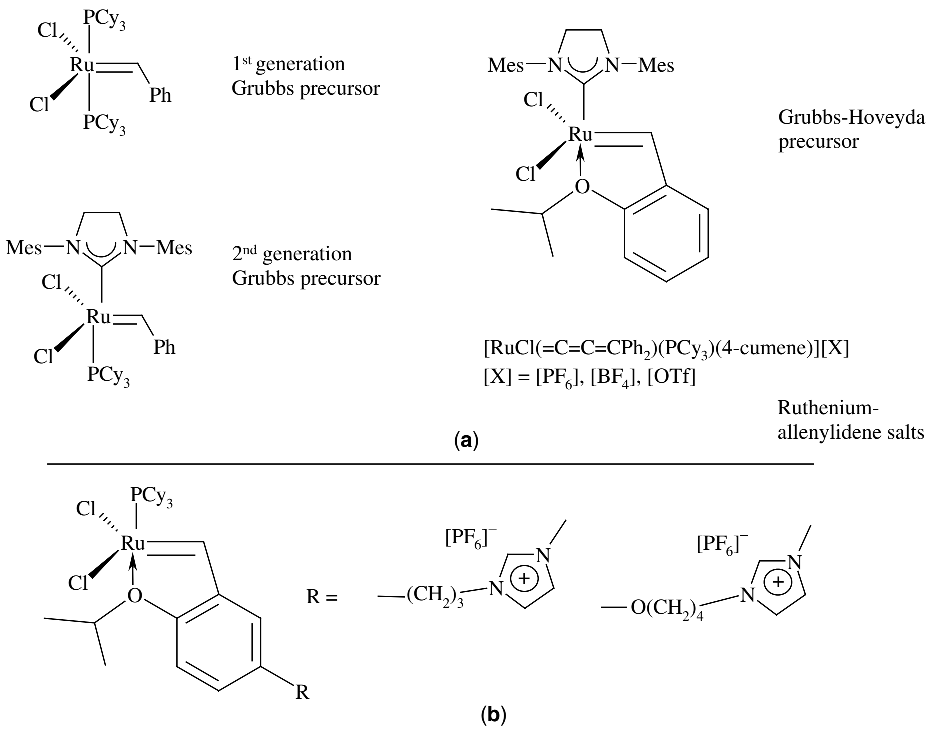
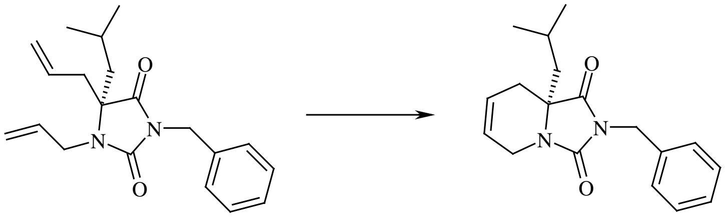


Fig. 22. First- and second-generation Grubbs precursors, Grubbs-Hoveyda precursor, Ru-allenylidene salts (**a**), and precursors bearing "ionic liquid tags" (**b**).

precursor, and three recycles were possible. However, the activity of the catalyst diminishes with each consecutive run (334). Mixtures of imidazolium-based ionic liquids were also tested. Although no trends can be derived from these results, the conversions and leaching varied depending on the mixture used (334). Ring-closing metathesis studied by Buijsman and co-workers (334) is shown in eq. 21.



(21)

Mayo *et al.* (335) investigated the ring-closing metathesis with both first-generation and second-generation Grubbs catalyst precursors in [C_4mim][BF_4] under microwave irradiation, with the goal of achieving shorter reaction times. With many substrates, conversions of 100% can be achieved after one minute of reaction time; however, the scale of the reaction is very small (20–40 μmol). This method is especially suitable for substrates which are thermally unstable; in such microwave experiments, the temperature of the reaction medium remains much lower during the reaction, whereas conventionally, the reagents are heated under reflux (335).

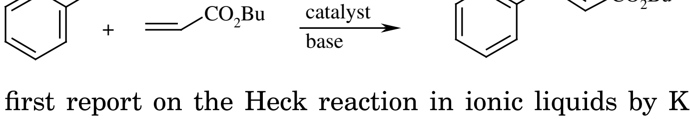
Stark and co-workers investigated both first- and second-generation Grubbs, and the Grubbs-Hoveyda catalyst precursors, on the model reaction of oct-1-ene to tetradec-7-ene and ethene. In addition to being oxygenate resistant, working at mild conditions, and giving high product linearities at moderate catalyst precursor cost, higher product selectivities are observed with ionic liquids than with either molecular solvents or the neat reaction (128).

Oliver-Bourbigou and co-workers investigated the ruthenium allenylidene salts shown in Figure 22 in 1-butyl-3-methylimidazolium salts (336). The ring closing metathesis with *N*,*N*-diallyl-4-methylbenzenesulfonamide to 1-[(4-methylphenyl) sulfonyl]-2,5-dihydro-1*H*-pyrrole proceeded within these systems, but slower than in toluene. The presence of $[BF_4]^-$ (either as counter-ion of the catalyst precursor and/or the ionic liquid) leads to the formation of side-products (up to 40%). Such behavior has been previously found in toluene. The best system in terms of selectivity and conversion is the precursor based on $[OTf]^-$ dissolved in $[C_4mim][OTf]$. However, the catalyst decomposes with time, making recycling not possible (336).

Comparison of the metathesis of *N*,*N*-diallyl-4-methylbenzenesulfonamide shows that in ionic liquids, the first-generation Grubbs catalyst precursor is approximately as effective as the $[OTf]^-$-based allenylidene salt, and similar turn-over frequencies can be achieved (335,336).

The very interesting concept of attaching an "ionic liquid tag" to catalyst ligands (see Fig. 22) was simultaneously pursued by the groups of Yao (337) and Guillemin (338). In the ring closing metathesis of *N*,*N*-diallyl-4-methylbenzenesulfonamide and other substrates, the use of these catalyst precursors significantly increased the recyclability of the system (337,338).

Coupling Reactions. Heck Reaction. The Heck reaction (339), which is a reaction between RX (where R = alkenyl or aryl, and X = halide or trifluoromethylsulfonate) and alkenes which do not possess any allylic hydrogen atoms, is one of the most important C-C coupling reactions and has been frequently investigated in ionic liquids (eq. 22). The catalyst palladium(0) is obtained by reduction of Pd(II)-salt/triphenylphosphine mixtures with triethylamine. Additionally, stoicheiometric amounts of base are necessary to quench any acid by-product (148). Conventionally, Heck reactions are performed in ethanenitrile or dimethylmethanamide. Although equimolar quantities of salt are produced, which have to be disposed of, this is an important reaction, since a wide range of functionalities are tolerated.



(22)

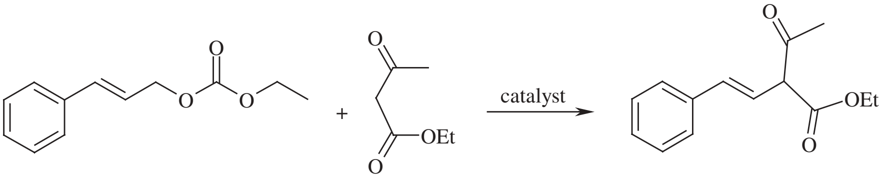
Since the first report on the Heck reaction in ionic liquids by Kaufmann *et al.* (340) in 1996, more than 150 publications have appeared on this topic up to Spring 2004. Intriguingly, seemingly contradictory results were published in the literature, and subsequently it became clear that halide anions, sometimes unintentionally present from the preparation of the ionic liquid, as well as carbenes formed from the imidazolium cation, may partake in the catalytic cycle (143,341). At least two mechanisms appear to be involved in the reaction involving a Pd(0)/Pd(II) or a Pd(II)/Pd(IV) catalyst cycle (342).

Thus, in ionic liquids with little coordinating ability of the anion, palladium black precipitates easily in the absence of triphenylphosphine. On the other hand, nucleophilic anions such as halides coordinate to the metal, thus maintaining a homogeneous solution. In imidazolium-based ionic liquids in the presence of chloride, metal complex solutions are formed which are not active in Heck reactions (343), while their bromide homologues are.

Pyridinium- or tetraalkylammonium-based ionic liquids, on the other side, are not able to form carbenes. In these instances, chloride forms the tetrachloropalladate(II) anion with the catalyst precursor, which promotes the Heck reaction (119,342–344). Kinetic studies indicate that the catalytically active species in such systems are palladium clusters, which are stabilized by the ionic liquid, therefore allowing for complete recyclability and product separation (343).

These combined research efforts have optimized the conditions to a level, at which “the ionic liquid process appears as one of the cleanest recyclable procedures so far described for the Heck reaction” (345).

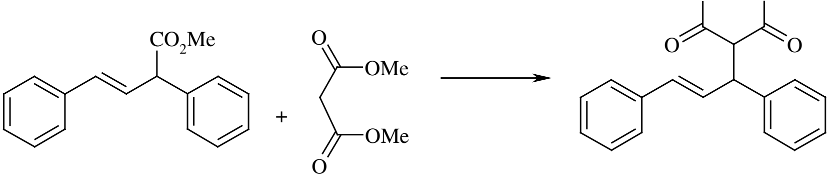
Trost-Tsuji and Related Coupling Reactions. The use of a biphasic [C_4mim]Cl-methylcyclohexane system in the Trost-Tsuji coupling reaction (346) (see eq. 23) of ethyl cinnamyl carbonate and ethyl acetoacetate with a catalyst derived from $PdCl_2$ and sodium triphenylphosphine trisulfonate (Na_3[tppts]), was compared to a water−butanenitrile system.



(23)

The reaction carried out in the aqueous phase suffers from drawbacks such as the formation of cinnamyl alcohol and tri(phenyl-3-sulfonate)cinnamyl phosphonium compounds. The former compound is a decomposition product of the substrate in the presence of water; the latter arise due to the high concentration of ligand necessary to achieve sufficient reaction rates in water (347). In the [C_4mim]Cl-methylcyclohexane system, on the other hand, the formation of both by-products is avoided, with the added advantage of higher catalyst efficiency. Also, facile separation of the product by decantation of the methylcyclohexane phase is possible (347).

Similarly, 3-acetoxy-1,3-diphenylprop-1-ene is quantitatively alkylated with dimethyl malonate in the presence of a palladium(II)—triphenylphosphine catalyst in [C_4mim][BF_4] in the presence of potassium carbonate at ambient temperature (eq. 24) (348).

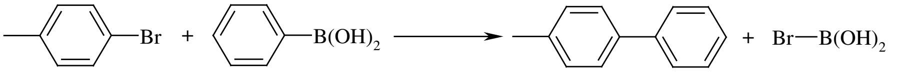


(24)

The presence of triphenylphosphine is a prerequisite for the reaction to occur, and the rate increases with the PPh_3-$Pd(O_2CCH_3)_2$ ratio (348). The same procedure can be used for the quantitative amination of 1,3-diphenylallyl acetate by pyrrolidine. Leaching is reduced when triphenylphosphine is replaced with Na_3[tppts] (where tppts = triphenylphosphine trisulfonate) (348). Xiao and co-workers investigated the effect of altering the phosphine ligands on this reaction, and found that electron-donating ones lead to faster reaction rates. Reactions in $[C_4mim][BF_4]$ are in general more efficient than when carried out in tetrahydrofuran (349).

Using *rac*-(E)-1,3-diphenyl-3-acetoxyprop-1-ene as substrate, the enantioselectivities of two ferrocenylphosphine ligands on palladium were tested in $[C_4mim][PF_6]$. High yields and high enantiomeric excesses of both the *R*- and the *S*-enantiomer can be obtained. However, the ligands are prone to leaching into the toluene phase, which is used to extract the product from the ionic liquid, thus leading to a decreased selectivity and yield (350).

Suzuki Cross-Coupling. The Suzuki coupling (351) of 4-bromotoluene with phenylboronic acid using the conventional $[Pd(PPh_3)_4]$ catalyst precursor was conducted in $[C_4mim][BF_4]$ (eq. 25). The reaction gives higher yields than when carried out in toluene, and an increase in reactivity at reduced catalyst concentrations is observed, even when nonactivated bromoarenes are used as substrate. The formation of homo-coupled side products is reduced to $<2\%$, and the recovered ionic liquid–catalyst mixture can be recycled. Additionally, small amounts of water increase the yield of 4-methylbiphenyl; this phenomenon can be attributed to the formation of the active species $[PhB(OH)_3]^-$, which then reacts with 4-bromotoluene (120,352). Chloride impurities lead to the deactivation of the catalyst (120); contrary to this, Welton and co-workers found that the addition of four equivalents of a halide source (eg, NaCl) to either preformed $[Pd(PPh_3)_4]$ or a mixture of $Pd(O_2CCH_3)_2$-PPh_3 prevented the decomposition of the palladium catalyst by formation of $[(PPh_3)_2Pd(C_4mimy)X]^+$ (where C_4mimy = 1-butyl-3-methylimidazolylidene) (353,354). This complex is extremely active in the Suzuki reaction, affording biphenyl in 95% yield from the coupling of bromobenzene with phenylboronic acid. No catalyst decomposition is observed, and consecutive catalytic runs are possible without loss in activity (353).

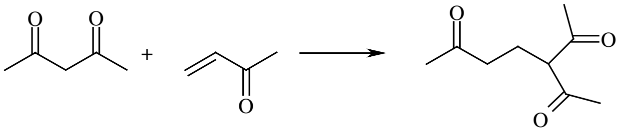


(25)

Sonogashira Coupling. The coupling of aryl halides and terminal alkyl- or aryl-alkynes has been studied in $[C_4mim][PF_6]$ (eq. 26) (355). The conventional palladium–copper-catalyzed reaction may also be carried out without the copper co-catalyst when $PdCl_2$-triphenylphosphine is used as the catalyst precursor in the presence of a base. The product is separated from the catalyst-containing ionic liquid phase by extraction with either diethyl ether or hexane, and the acid–base adduct removed with water. The remaining ionic liquid–catalyst solution can be recycled several times with little loss of catalytic activity, and a microflow reaction system can also be used for this reaction (355). This reaction has now been commercialized by the Central Glass Company of Japan (see also Section 12) for preparing pharmaceutical intermediates.

$$\mathrm{R{-}X} + \mathrm{H{-}{\equiv}{-}R'} \longrightarrow \mathrm{R{-}{\equiv}{-}R'} \qquad (26)$$

Michael Addition. The Michael addition of pentane-2,4-dione to methyl vinyl ketone (see eq. 27), catalysed by nickel(II), iron(III) or ytterbium(III), was investigated in [C_4mim][BF_4], and nickel(II) was found to give the best performance in terms of activity. This system is recyclable for at least eight times, with selectivity $>98\%$. Higher conversions are achieved in the ionic liquid system than in dioxane (356).



(27)

Other Coupling Reactions. The Stille reaction (cross-coupling reaction of aryl halides with organostannanes to yield substituted biphenyls in the presence of a palladium(II) catalyst precursor) (357) and related coupling reactions (316,358) have been investigated. However, these reactions produce metal-containing by-products in equimolar quantities and are thus neither economic nor benign.

Friedel-Crafts and Diels-Alder Reactions. Due to their tuneable Lewis acidity, Friedel-Crafts and Diels-Alder reactions were obvious reactions to be investigated in the first-generation chloroaluminate ionic liquids. Unfortunately, the moisture sensitivity of the Lewis acidic species, as well as their strong coordination with any Lewis basic sites of the substrate (such as carbonyl groups of products in the Friedel-Crafts acylation) leads to a stoicheiometric reaction (10). In fact, in such an ionic liquid, even more $Al(OH)_3$-waste is created after quenching than conventionally, due to the extra aluminium(III) chloride required for the make-up of the ionic liquid. However, if the analogous indium(III) system is used, many of these problems may be circumvented (359).

Friedel-Crafts Reactions. The problem of strong Lewis acid-carbonyl coordination is overcome by using trifluoromethyl sulfonate salts as catalyst. Thus, the Friedel-Crafts acylation (360) of anisole with benzoyl chloride in [C_4mim][BF_4] with copper(II), zinc(II), tin(II) or scandium(III) trifluoromethylsulfonates shows that $Cu(OTf)_2$ gives the highest conversion with high *para*-selectivity. The reactions with the other trifluoromethylsulfonates also proceed to completion. The reactivity and selectivity of the $Cu(OTf)_2$-ionic liquid systems are higher than when the reaction is performed in either ethanenitrile or 1,2-dichloroethane. Substituting acyl chloride for the corresponding anhydride reduces the yield, although similar selectivities are obtained. The recycling of the solvent/catalyst system is feasible for at least three cycles; the conversions decrease slowly, while the selectivity remains constant throughout the runs. It was suggested that accumulating amounts of HCl in the reaction mixture lead to the formation of $CuCl_2$, thus deactivating the catalyst. Another interesting finding is the formation of the kinetic product 1-(2-methoxynaphthyl) phenyl ketone in the benzoylation of 2-methoxynaphthalene. Under conventional reaction conditions, this product undergoes isomerization to 2-(6-methoxynaphthyl) phenyl ketone; not so in the ionic liquid, even after prolonged reaction. Such behavior was previously found in the acetylation of naphthalene, where the thermodynamically unfavored 1-isomer is obtained in [C_2mim]-based chloroaluminates (10). Additionally, the benzoylation of 2-methoxybiphenyl gives selectively 2-methoxy-2′-benzoyl-biphenyl in the ionic liquid, whereas in a conventional solvent, the benzoylation occurs *para* to the methoxy group. Overall, this methodology provides an excellent alternative to acylations conducted with aluminium(III) chloride (360). Bis{(trifluoromethyl)sulfonyl}amide salts and complexes were also reported as outstanding catalysts in Friedel-Crafts acylation reactions. Additionally, recycling of both the catalyst and the ionic liquid is possible, and the reaction proceeds with a high turn-over number (361).

Strong catalyst-product coordination does not occur in Friedel-Crafts alkylations, and first-generation ionic liquids have been shown to be in very effective catalysts (9,10). In these systems, the alkylbenzenes form a second layer over the ionic liquid phase, and recycling is easily feasible with little leaching (12). Such alkylations can also be carried out with water-stable (and therefore recoverable) scandium(III) trifluoromethylsulfonate (362). For example, this catalyst can be used in the alkylation of benzene with hex-1-ene in hydrophobic ionic liquids such as [C_2mim][SbF_6], [C_4mim][PF_6] or [C_4mim][SbF_6]. Interestingly, this reaction does not proceed in molecular solvents, such as dichloromethane, water, ethanenitrile or nitromethane. Likewise the reaction does not take place in water-soluble ionic liquids, such as [C_2mim][BF_4] and [C_4mim][BF_4] (363). This could be due to chloride-contamination, as well as high water-contents of these ionic liquids. The water-immiscible ionic liquids and the catalyst, however, are recyclable by decanting the insoluble, lighter, product-containing phase from the ionic liquid. No loss of activity is observed in the recycle runs (363).

Diels-Alder Reactions. The first Diels-Alder reaction in ionic liquids was reported as early as 1989 (364), when ethylammonium nitrate (mp 12°C) was used as solvent in absence of any metal catalyst. A higher *endo*-stereoselectivity is observed in the reaction of cyclopentadiene with methyl acrylate or methyl vinyl ketone than when the reaction is carried out in either benzene or ethanol, but lower than when water is used as solvent. The *endo*/*exo* ratio corresponds approximately to the one obtained in either methanol or formamide (Fig. 10) (364).

The reaction was further investigated in 1,3-dialkylimidazolium-, phosphonium- and quaternary ammonium-based ionic liquids; a high *endo*/*exo* ratio is observed (dependent upon anion) and the ionic liquids are recyclable (81,365). More recently, it was found that the addition of scandium trifluoromethylsulfonate to either [C_4mim][PF_6], [C_4mim][SbF_6] or [C_4mim][OTf] leads to very high *endo*/*exo* ratios (>99) in the reaction of 1,4-naphthoquinone with 1,3-dimethylbutadiene with improved reaction rates. Furthermore, the counter anion does not alter the reaction outcome, and recycling is possible for ten cycles (366).

In the platinum(II)-catalyzed reaction of cyclopentadiene and acryloyl-*N*-oxazolidinone, the presence of an ionic liquid improves the catalyst stability, thus leading to higher reaction rates. Additional advantages include facile catalyst recycling and high enantioselectivities (367).

Oxidation. Until 2000, there were no reports in the literature of chemical oxidation processes carried out in ionic liquids. However, industrially performed catalytic oxidation reactions often suffer from drawbacks such as low atom-efficiency and poor selectivity, corrosive reaction media, lack of solvent and catalyst recycling, and negative environmental impact due to evaporation of the solvents (368). The selective catalytic oxidation, eg, toluene to benzaldehyde, is a major challenge for industry, not only because of the above-mentioned problems, but also because of the formation of side-products due to over-oxidation. Thus, if the oxidation of toluene is performed in liquid phase, benzoic acid is also formed. In the gaseous phase, decomposition to carbon dioxide frequently occurs, and such reactions are hence traditionally performed at very low conversion rates (369).

Oxidation of Aromatic Aldehydes. The oxidation of aromatic aldehydes by O_2 in $[C_4mim][PF_6]$ was reported by Howarth (370). The reaction, which is catalysed by 3 mol% $Ni(acac)_2$ (where Hacac = pentane-2,4-dione) gave moderate to good yields. Leaching of the catalyst was observed during the extraction of the product with ethyl ethanoate, and recycling of the ionic liquid-catalyst phase was feasible (370).

Oxidation of Alcohols and Alkylbenzenes. Ley and co-workers (371) reported the oxidation of alcohols with tetrapropylammonium ruthenate(VII) (10 mol%) in a mixture of dichloromethane and either $[C_2mim][PF_6]$ or $[Et_4N]Br$, with *N*-methylmorpholine-*N*′-oxide as oxidant. The recycling of the ionic liquid–catalyst mixture is feasible for five cycles: recovery is achieved by addition of diethyl ether, which causes the precipitation of the ionic liquid. The ionic liquid is used not as a solvent, but as a means for recovery of the catalyst; in fact, the mixing of neat ionic liquids and the catalyst precursor leads to a violent and exothermic reaction, in which the ionic liquid is destroyed (371).

Farmer and Welton (104), on the other hand, used a similar system without the addition of dichloromethane. However, they reported that the ionic liquid needs to be free of chloride impurities, as well as the unknown yellow tint, in order to achieve repeatable results. Although the reaction generally proceeds slower than in dichloromethane, benzylic and allylic alcohols are selectively oxidized to the corresponding aldehydes or ketones. No overoxidation to the acids is observed, even in presence of one equivalent of water. This is attributed to an association of the water to the anions (103) of the ionic liquid, thus preventing the contact of the catalyst with water.

Furthermore, tetrapropylammonium ruthenate(VII) can be used in conjunction with O_2 and CuCl and/or 2-aminopyridine as co-catalysts in the oxidation of benzylic alcohols. Without the co-catalysts, the conversion of benzyl alcohol is very low, but excellent conversions are achieved by adding both co-catalysts. Under similar conditions, conversions are comparable to when the reaction is carried out in dichloromethane. Oxidation of the imidazolium cation to 1-butyl-3-methylimidazolidone and 1-butyl-3-methyl-2,4,5-trione is also observed, which can be prevented by using the C-2 protected 1-butyl-2,3-dimethyl-imidazolium derivative. Decent results are also obtained in the absence of 2-aminopyridine. No account is given as to the recyclability of the system (104).

The selective oxidation of benzyl alcohol to benzaldehyde, using $Pd(O_2CCH_3)_2$ as a catalyst precursor and air or pure O_2 as terminal oxidant, was used as an example to show that [C_4mim][BF_4] gives better reaction rates than conventionally used dimethyl sulfoxide, with the added advantage of facile catalyst and solvent recycling (123). The activity and selectivity are dependent on two factors: firstly, the presence of chloride ions (either as counter ion of the ionic liquid or as impurity from its preparation) leads to the formation of dibenzyl ether as a side-product. This finding is possibly due to the formation of homogeneously dissolved $[PdCl_4]^{2-}$. In halide-free ionic liquids, palladium metal precipitated during the course of the reaction, which is the catalytic species. Secondly, the presence of an excess of water relative to ionic liquid leads to the overoxidation to benzoic acid. However, in sub-stoicheiometric amounts, water appears to be deactivated by the ionic liquid (123), possibly by a similar mechanism to that observed by Farmer and Welton (*vide supra*) (103,104). In recycling experiments, accumulating amounts of water (generated from the reaction, or from absorption from the atmosphere) lead to the formation of benzoic acid (Fig. 23). However, occasional drying of the ionic liquid between runs affords a selective, recyclable system (123).

Alternatively, alcohols can be selectively oxidized to aldehydes or ketones using a homogeneous mixture of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and CuCl in [C_4mim][PF_6] at 65°C, using O_2 as terminal oxidant. The product was extracted with diethyl ether. Recycling of the ionic liquids is feasible for at least eight cycles if the ionic liquid–catalyst mixture is washed with water and dried at elevated temperatures *in vacuo*. Unfortunately, the catalyst is lost during this procedure, and further studies are necessary to allow for the recycling of the catalyst (372).

Preliminary results (123) show that the introduction of oxygen into the molecule (as opposed to dehydrogenation of alcohols) is also feasible in an ionic liquid. Toluene gives low conversions in this unoptimized system. However, ethylbenzene is oxidized to acetophenone in high yields, which compare well with results obtained in conventionally used solvent systems (123).

In the oxidation of styrene to acetophenone with H_2O_2 and $PdCl_2$ at 60°C (Wacker-type reaction), the presence of small amounts of either [C_4mim][BF_4]

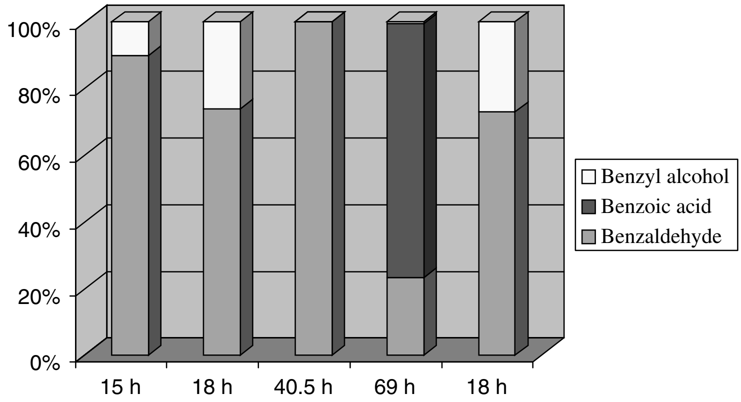


Fig. 23. Recycling experiments of the oxidation of benzyl alcohol and dependence of selectivity on water content (123).

or [C_4mim][PF_6] increases the reaction rate. 100% conversion is achieved within 3 h, with only 1.15 equivalent excess of H_2O_2; however, about 10% side-products (benzaldehyde and benzoic acid) are formed, and recycling is not reported (373).

Epoxidation. The epoxidation of an array of alkenes and allylic alcohols has been achieved with urea–H_2O_2 in [C_2mim][BF_4], using methyltrioxorhenium(VII) as catalyst precursor, at room temperature (125,374). Under these conditions, the reaction mixture is a homogeneous system, from which the product is extracted with diethyl ether. The authors state that the selectivity to the epoxide is >95%, since epoxide cleavage under formation of diols does not occur in anhydrous solvents, such as a dry ionic liquid. This observation has also been made in the metal-free epoxidation of electrophilic alkenes in biphasic mode (375). Compared to $CHCl_3$, [C_2mim][BF_4] leads to higher reaction rates, due to better solubility of the urea–H_2O_2 in ionic liquids. The authors also point out the negative effect of both residual halide and unreacted pyridine or 1-methylimidazole in the ionic liquid, leading to side-product formation (125,374).

The chiral epoxidation of diverse alkenes by Jacobsen's chiral catalyst, [*N,N'*-{bis(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediamine}manganese(III)] chloride, with aqueous NaOCl as oxidant at 0°C, was reported by Song and Roh (121). This reaction is performed in a mixture of [C_4mim][PF_6] and dichloromethane as opposed to the pure ionic liquid. The role of the ionic liquid is the immobilization of the catalyst; during the reaction, the catalyst forms a heterogeneous liquid–liquid mixture with the solvents and the reactant. After the reaction, the aqueous phase is separated from the organic phase, and the dichloromethane removed *in vacuo*. The residue contains the catalyst, the ionic liquid and the product, which is extracted with hexane. The catalyst-containing ionic liquid is reused in subsequent runs, where the catalytic activity and selectivity decreases gradually, due either to leaching, degradation, or to physical loss of the catalyst. The disadvantages of this method however are clear: the use of the very volatile dichloromethane in a benign process is a contradiction. Additionally, the use of NaOCl as oxidant produces equimolar amounts of NaCl as by-product and is therefore not atom-efficient. However, Gaillon and Bedioui have shown by electrochemical analysis that the activation of O_2 by Jacobsen's catalyst is feasible. Thus, NaOCl may possibly be replaced by O_2 (376).

Nitration. The "greening" of one of the most environmentally harmful reactions, the nitration of aromatic substrates by stoicheiometric amounts of nitric acid, has been investigated by Handy and Egrie using ytterbium(III) or copper(II) trifluoromethylsulfonate in ionic liquids (377). This approach avoids the use of water-sensitive and toxic reagents and the generation of large amounts of highly acidic and water-reactive wastes. Although ytterbium(III) trifluoromethylsulfonate can be used and recycled in dichloroethane, it is necessary to dry the catalyst prior to reuse. Performing the reaction in an ionic liquid makes this drying process and the use of dichloroethane superfluous.

The choice of the ionic liquid solvent for the nitration is of utmost importance: imidazolium-based ionic liquids are nitrated at the cationic aromatic ring. Therefore, for the nitration of toluene and other aromatic substrates, 1-butyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}amide was selected, which is resistant against nitration. Thus, toluene reacts with 1 equivalent of nitric acid in the presence of ytterbium(III) trifluoromethylsulfonate to give nitrotoluenes in 95% yield. The distribution of the isomers is similar to that observed in conventional solvents. Electron-deficient substrates, however, give very poor yields under these conditions, but the addition of trifluoroethanoic anhydride to generate trifluoroacetyl nitrate *in situ* circumvents this problem. Thus, bromobenzene is nitrated in good yields. Surprisingly, the much less expensive copper(II) trifluoromethylsulfonate also gives similarly high yields. Both catalyst-ionic liquid systems allow for recycling (at least four times) by either extraction of the products or distillation (377).

Nucleophilic Aromatic Substitution. Various 1-butyl-3-methylimidazolium-based halides were tested in the catalytic substitution of aromatic halides with cyanide (the Rosenmund-von Braun reaction). It was found that CuI can be used in the presence of NaCN to bring about the complete conversion of 2-iodonaphthalene and other substrates. Recycling is possible after extraction of the products, but no account is given regarding the removal of the by-product NaX from the reaction mixture (378).

11.4. Biocatalysis. Since the first investigation of biocatalytic reactions in ionic liquids (265,379,380), various studies have been conducted, which have been recently reviewed (381). One of the overall conclusions is that biocatalytic reactions proceed somewhat less efficiently in ionic liquids than in water, but better than in organic solvents. Especially for water-sensitive substrates, ionic liquids offer some potential in biocatalysis.

Whole-cell Systems. Ionic liquids have been used as substitutes for organic solvents in organic-aqueous biphasic biotransformations. Biphasic reaction conditions are traditionally used if the substrate is poorly water-soluble or toxic to the biocatalyst's cell membrane at high concentrations. The organic solvent then acts as a substrate reservoir, which constantly releases reactant to the biocatalyst. However, organic solvents are often toxic, as well as being volatile and flammable. Lye and co-workers (265) substituted toluene with $[C_4mim][PF_6]$ as a reservoir for 1,3-dicyanobenzene, which is converted to 3-cyanobenzamide and 3-cyanobenzoic acid by *rhodococcus* bacteria in an aqueous buffer solution. It was found that the ionic liquid is compatible with the cells, and the transformation profiles were similar in both systems (265,382). Similar observations were made when *lactobacillus kefir* was used for the asymmetric reduction of 4-chloroacetophenone to *R*-1-(4-chlorophenyl)ethanol in a biphasic water-$[C_4mim][NTf_2]$ system (383).

Free Enzyme-catalyzed Reactions. The lipase-catalyzed (*Candida Antarctica*) alcoholysis, ammoniolysis and perhydrolysis can be performed in pure ionic liquids under very mild conditions (124,379). Similarly, $[C_4mim][PF_6]$ can also be used as the sole solvent in the thermolysin-catalysed reaction of carbobenzoxy-*L*-aspartate and *L*-phenylalanine methyl ester hydrochloride to *Z*-aspartame (384). In the ammoniolysis of ethyl octanoate with various lipase forms in $[C_4mim][BF_4]$, the activity of the system is lower than that in $(CH_3)_3COH$. On the other hand, the condensation of a carboxylic acid and ammonia by Novozym 435 is achieved with better reaction rates in the ionic liquid than in methyl isobutyl ketone. Using the same lipase, it is possible to oxidize cyclohexene to yield the epoxide *via* the intermediate peroctanoic acid from octanoic acid and H_2O_2. In this case, the conversion is only slightly lower than that achieved under optimal conditions in ethanenitrile, and the ionic liquid does not affect the stability of the biocatalyst. As in organic solvents, the reactivity of the immobilized lipase is generally higher than that of the free enzyme (379).

Higher enantiomeric excesses are obtained in the lipase-catalysed transesterification of various alcohols with esters (124,262,385,386) carried out in various ionic liquids, when compared to conventional solvents. This finding was attributed to interactions of the ionic liquid with the enzyme, altering the selectivity of a biocatalytic reaction. Additionally, Itoh and co-workers (386) and Kim *et al.* (387) achieved high enantioselectivities (>99% selectivity), and the ionic liquid and enzyme were recyclable for five times after extracting the product from the ionic liquid phase with diethyl ether (386). A recycling process for the continuous extraction of the product with supercritical CO_2 was also reported (262,388).

In an extensive study, chloride, acid and/or silver impurities were found to be responsible for a decrease in reaction rate. In pure ionic liquids, the rate of lipase-catalysed reactions is dependent on the solvent polarity, as determined by Reichardt's dye: although in organic solvents, better reaction rates are achieved in nonpolar solvents such as toluene, highly polar ionic liquids gave better conversions than less polar ones (389). The coordinating properties of the anion of the ionic liquid also play an important part in influencing the enzymes' activity: no conversion takes place in $[C_4mim][NO_3]$, $[C_4mim]$[lactate], $[C_2mim][EtSO_4]$ and $[EtNH_3][NO_3]$, whereas ionic liquids with anions such as tetrafluoroborate or trifluoromethylsulfonate give similar or higher conversions and selectivities to $(CH_3)_3COH$ (124).

α-Chymotrypsin-catalyzed reactions were investigated by several groups in 2001 (261,262,388). Laszlo and Compton describe the transesterification of *N*-acetyl-*L*-phenylalanine ethyl ester with propan-1-ol in $[C_4mim][PF_6]$ and $[C_8mim][PF_6]$. Apart from the enzyme formulation, the reaction is dependent on the polarity of the solvent, and gives better conversions in the less polar $[C_8mim][PF_6]$ than in $[C_4mim][PF_6]$. Thus, similar results are achieved as in such nonpolar solvents as hexane and isooctane. However, as in other relatively polar organic solvents, the addition of traces of water was necessary to achieve enzyme activity unless supercritical CO_2 is used for the extraction and recovery of product and substrate (261,388). A dependency on the polarity and viscosity of the ionic liquid in the synthesis of *N*-acetyl-*L*-tyrosine propyl ester was also observed by Vaultier and co-workers (262). These authors also found that the less polar ionic liquids reduce the activity of the enzyme. Although this result stands in contrast to the results obtained by Laszlo and Compton (261), inconsistencies between different studies may be due varying enzyme formulation as well as ionic liquid preparation and impurity levels (262).

There have also been reports of biocatalytic reactions carried out in ionic liquids, from which the products are removed after the reaction using supercritical fluids (261,262,390). These publications illustrate that catalyst and ionic liquid recycling are feasible using this method.

11.5. Conclusions. In the majority of the above examples of catalysis, ionic liquids have demonstrated that they can be used as effective, environmentally benign solvents for clean chemical reactions. As such, they can act as replacements for volatile organic solvents, whether being utilized in the laboratory or on an industrial scale. Besides performing as solvents, some ionic liquids have been shown to exhibit a pronounced effect on the reaction outcome. Thus, the solvent properties as well as the ability to participate in the formation of the catalytically active species can be fine-tuned by deliberate choice of the ionic liquid. Unusual reaction pathways are anticipated in some instances.

The effect of the ionic liquid upon the outcome of a reaction is actually best illustrated by an archetypal noncatalytic example (297). If toluene and nitric acid are allowed to react in a halide-based ionic liquid, near-quantitative yields of halotoluene are obtained; in a triflate-based ionic liquid, similar yields of nitrotoluene are isolated; in a mesylate-based ionic liquid, near-quantitative yields of benzoic acid are produced. Three different ionic liquids and the same reagents – three different outcomes, and no cross-contamination of products!

Besides frequently observed increases in yields or higher selectivity, the most important development is the principle of the "immobilization" of the catalyst, which in many cases is homogeneously dissolved in the ionic liquid. Hence, the advantages of homogenous and heterogeneous catalysis are combined in a biphasic system.

The unique physical properties of ionic liquids, such as their negligible vapor pressure, density and solvent properties, lend themselves perfectly to the design of suitable reaction and separation equipment. Due to these properties, the separation of many compounds may be achieved by simple phase separation. This concept has already been put into practice on an industrial scale in the BASIL process (391). Miscible, but volatile compounds can be removed from the reaction mixture by distillation, leaving the catalyst-ionic liquid mixture behind for recycling. At present, in most academic publications, products are removed by extraction with organic solvents, since in the laboratory extraction is easier and faster to carry out. In the near future, the extraction with organic solvents should be substituted by other, more ecologically sound methods, eg, by using supercritical fluids or water, or pervaporation techniques (392). Additionally, the extraction with organic solvents occasionally leads to metal leaching, especially when neutral ligands are present. New, carefully designed, catalytic systems are currently being investigated to avoid this problem.

12. Industrial Applications

The huge industrial interest in ionic liquids is reflected in the patent literature (42,62,306,307,309,313,393,394), but, to-date, only few processes have reached commercialization. A review of the industrial chemistry of ionic liquids will be published in the near future (395).

The first ionic liquid process which was developed to be implemented in existing technology is the Difasol process of the Institut Français du Pétrole. The nickel-catalyzed dimerization is carried out in Lewis acidic organochloroaluminate ionic liquids, in a continuously run biphasic mode. Organochloroaluminate ionic liquids are derivatives of the first-generation ionic liquids, eg, $[C_4mim][Al_2Cl_5Et_2]$. In this reaction, the product phase is insoluble in the catalyst-containing ionic liquid phase. The separation of the product is thus facilitated and the catalyst can be reused (15). Furthermore, the selectivity to dimers is improved when compared to the conventional Dimersol process, and the catalyst is used more efficiently.

Newer developments include a process for the synthesis of organo-modified siloxane polymers via a hydrosilylation route, developed by Degussa AG. The products are used in a number of industrial applications, such as stabilizers for polyurethane foams, antifoaming agents, and emulsifiers. The ionic liquid serves as a solvent for the platinum catalyst, which can be easily recycled. Another sector of interests is the use of ionic liquids as secondary stabilizer in universal pigment pastes for all kinds of varnishes and coatings, reducing the consumption of volatile organic solvents. Finally, the use of ionic liquids as electrolytes in lithium-ion batteries has been investigated. Conventionally, organic solvents such as ethene carbonate and dimethyl carbonate, together with lithium hexafluorophosphate, are used to produce batteries with high charge density. However, under extreme temperature conditions, the performance of the electrolyte decreases, and improper handling of the charging process can lead to safety issues. The use of ionic liquids addresses these problems (396).

ExxonMobil employs conventional rhodium catalysis for the biphasic carbonylation in Lewis-acidic ionic liquids (394). In the BASIL^{TM} (Biphasic Acid Scavenging Utilising Ionic Liquids) process by BASF AG, 1-methylimidazole is used as a base to neutralize acid liberated during the reaction of phenylchlorophosphines with alcohols to yield alkyoxyphenylphosphines, used as photoinitiators in the manufacture of printing inks, glass fiber and wood coatings (391,397). As opposed to the old process, which employed a tertiary amine, a protonated ionic liquid (1-*H*-3-methylimidazolium chloride) is formed, which can be easily phase-separated from the product, making time-consuming filtration steps superfluous. Additionally, the space-time yield is increased from 8 kg m^{-3} h^{-1} to 690,000 kg m^{-3} h^{-1} using the BASIL^{TM} process, and the yield increased from 50% to 98%. 1-Methylimidazole is recycled by thermal decomposition of 1-*H*-3-methylimidazolium chloride (391,398).

Eli Lilly and Company showed that molten pyridinium chloride can be used on multikilogram scale to demethylate 4-methoxyphenylbutanoic acid to 4-hydroxyphenylbutanoic acid, a precursor in the manufacture of a preclinical candidate (399).

13. Conclusions and Future Challenges

Although ionic liquids have received enormous attention in the literature (see Fig. 24) and hold a great potential for improving industrial processes ecologically or economically, there are three main issues which have to be addressed soon to quicken their (already impressively fast) implementation in industry.

Firstly, there is still a lack of reliable physical data, due to the fact that the purity of ionic liquids (Section 6) has only recently been recognized to be of utmost importance for any measurements. However, IUPAC have created a freely accessible database of physical and thermochemical properties (155,401), which will enable rapid testing and retrieval of extant data.

The second issue, which hampers a widespread use as industrial solvents, arises from the obvious current deficiency of toxicological and ecotoxicological data (Section 9), and only one preliminary study has dealt with the life-cycle assessment of ionic liquids to date (402). Obtaining toxicological data is costly,

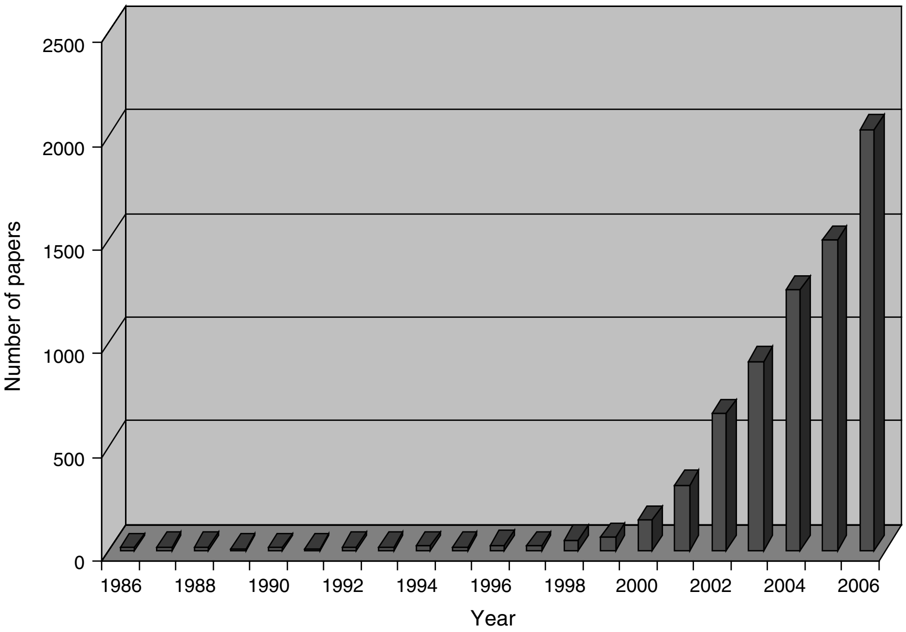


Fig. 24. Publications containing the phrase "ionic liquid" in the title, abstract or keywords, determined using SciFinder, as a function of time 1986–2006 (400).

and the sheer number of ionic liquids complicates premarketing notification processes, since most ionic liquids are not included in the European Inventory of Existing Chemical Substances (EINECS). Also, the question of how ionic liquids are to be disposed off has not been fully addressed.

The final issue is the growing mythology about ionic liquids–ingrained assumptions about them which people believe, but have no reason to believe. This problem has been dealt with elsewhere (403).

Nevertheless, a huge step towards the industrial use of ionic liquids has been taken in the last five years, when the first ionic liquids became commercially available from companies such as Merck, Cytec, SACHEM, DuPont, BASF, Fluka, Solchemar, Scionix, Solvent Innovation, Acros, Chemada, Degussa, etc, and a number are already available on the multi-ton scale.

At this point the obvious is emphasized: with over 6000 papers on ionic liquids published in the past ten years, this article has not attempted to give comprehensive coverage. Instead, the authors highlighted what they consider to be the important properties and chemistry of ionic liquids, including references to many recent reviews and key papers, allowing the interested reader to do their own data mining with a good grounding in the basics. The history of ionic liquid research shows a development at an interface between industrial and academic collaboration, in the fields of chemistry, engineering and catalysis. These collaborations are facilitated by academic research centres with industrial sponsorship, such as QUILL at the Queen's University of Belfast and the Centre for Green Manufacturing at the University of Alabama. QUILL, indeed, has published two reports aimed at providing general information on both the industrialization of ionic liquids (243), and sourcing them (107). Typically, processes take 10–15 years to move from initial experiments to industrial plant; with ionic liquids, this transition is being made in 3–4 years. The next decade of ionic liquid research should be even more fascinating and fruitful than the last one.

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