Chapter 1
Ionic Liquids as Green Solvents: Progress and Prospects

Shadpour Mallakpour and Mohammad Dinari

Abstract Volatile organic solvents (VOS) creating increasing air pollution are common reaction media for many chemical processes. VOS cannot be easily separated from the desired reaction products and difficult to recycle. In view of awareness of the deteriorating environment, researches are directed on developing alternative environmental friendly solvent systems to replace traditional volatile organics. Within this context, the interest of ionic liquids (ILs) as "green" solvents resides in their extremely low vapor pressure and high thermal stability, which offers advantages such as ease of containment, product recovery, and recycling ability. In addition, ILs show considerable variation in their stability to moisture and their miscibility with molecular liquids. Properties such as density, melting point, water and cosolvent miscibility, viscosity, polarity, acid/base character, and coordinating ability can be tailored by the appropriate selection of the cation and/or anion component. ILs have been implemented as solvent systems in chemical reactions, separations, extractions, electroanalytical applications and chemical sensing, among many others. Also, they have high ionic character that enhances the reaction rates to a great extent in many reactions. These features allow ILs to be used as potential alternative solvents to VOS in a wide variety of industrial chemical processes. Furthermore, the use of ILs as industrial solvents can result in economical, social, and ecological impact due to their effect on the human health and environment.

S. Mallakpour (✉)
Organic Polymer Chemistry Research Laboratory, Department of Chemistry,
Isfahan University of Technology, Isfahan, Iran

Nanotechnology and Advanced Materials Institute, Isfahan University of Technology,
Isfahan, Iran
e-mail: mallak@cc.iut.ac.ir; mallak777@yahoo.com; mallakpour84@alumni.ufl.edu

M. Dinari
Organic Polymer Chemistry Research Laboratory, Department of Chemistry,
Isfahan University of Technology, Isfahan, Iran

1.1 Introduction

Solvents are high on the list of damaging chemicals for two simple reasons: (a) they are used in large quantity and (b) they are usually volatile liquids. Volatile organic solvents, which have caused concerns on increasing air pollution and worker's health, are common reaction media for commercial production of different chemicals. It is an enormous challenge to reduce the amount of volatile organic compounds (VOCs) used in chemical and industrial processes. Governmental policies for the control of emissions of different substances which are released into the environment will become more restrictive as pollution increases worldwide. Therefore, the development of more efficient and environmentally friendly processes will be obligatory in the coming years [1–6]. These developments must be designed on the basis of two main characteristics: energy saving to avoid excessive emission of carbon dioxide (CO_2) and reduction of emissions related to harmful VOCs. Research on chemical manufacturing has focused on the investigation of different approaches for diminishing the emission of VOCs including solvent-free processes and the use of water, supercritical CO_2, and, more recently, ionic liquids (ILs) as the reaction media [7–10]. Among solvents, ILs have been rather sanguinely viewed as environmentally friendly or "green" solvents. Because of multiplicity of their uses, attention in ILs suddenly increased. ILs are organic salts that are liquid at ambient temperatures, preferably at room temperature. The reason why ILs are liquid at room temperature is still not fully understood. From recent X-ray crystal structure studies, we know that some of these tend to crystallize into disordered solids, and, depending upon the rate of cooling, crystal polymorphism can be observed. On the basis of these observations, it has been speculated that the gain in energy upon formation of the crystal is not as large as in traditional inorganic salts and is not enough to compensate for the loss in entropy that accompanies the formation of the crystal at room temperature. Experiments show that several of these systems have a tendency toward glassy behavior, and, depending upon the length of alkyl substituents in the cations, their properties range from those of normal liquids to glassy or even liquid crystals [11]. There are many synonyms including ionic fluid, molten salt, liquid organic salt, fused salt, or neoteric solvent [12–15] that used for ILs, which can complicate a literature search. "Molten salts" is the most common and most broadly applied term for ionic compounds in the liquid state. It appears that the difference between ILs and molten salts is just a matter of degree; however, the practical differences are sufficient to justify a separately identified niche for the salts that are liquid around room temperature.

Some useful properties of ILs are as following: they are relatively nonvolatile, which means they do not produce atmospheric VOCs and can be used in low-pressure environments. They possess good thermal stability and do not decompose over a large temperature range, thereby making it feasible to carry out reactions requiring high temperature conveniently in ILs. They can be considered both a polar and a noncoordinating solvents and show a high degree of

potential for enantioselective reactions as a significant impact on the reactivities and selectivities. Chiral ILs have been used to control the stereoselectivity. ILs are complex and versatile solvents capable to interact via hydrogen bonding, π–π, n–π, dispersive, dipolar, electrostatic, and hydrophobic interactions and serve as a good medium to solubilize gases such as H_2, CO, O_2, and CO_2. Many reactions are now being performed using ILs and supercritical CO_2. They can be immiscible with nonpolar organic solvents and/or water. ILs have high ionic character that enhances the reaction rates to a great extent in many reactions including microwave-assisted organic synthesis as well as polymerization reactions. The solubility of ILs depends upon the nature of the cations and counter anions. They have physicochemical properties that can be controlled by judicious selection of the cation and/or anion. Many of them can be stored without decomposition for a long period of time [16–27].

There are several important review articles on the synthesis, properties, and applications of room temperature ILs (RTILs), including solvents for synthesis and catalysis [28], ILs – new solutions for transition metal catalysis [29], a short history of ILs [30], IL (molten salt) phase organometallic catalysis [12], RTILs as replacements for conventional solvents [31], biocatalysis in ILs – advantages beyond green technology [32], ILs and chirality: opportunities and challenges [33], biocatalytic transformations in ILs [34], application of ILs as solvents for polymerization processes [35], chromatographic and spectroscopic methods for the determination of solvent properties of RTILs [36], development of ILs as green reaction media and catalysts [37], ILs for the convenient synthesis of functional nanoparticles and other inorganic nanostructures [38], ILs in catalysis [39], non-haloaluminate RTILs in electrochemistry [40], task-specific ILs (TSILs) [41], application of ILs in analytical chemistry [42], biodegradable ILs [43], chiral ILs: synthesis and applications [20], effect of ions and other compatible solutes on enzyme activity and its implication for biocatalysis using ILs [44], IL crystals [25], ILs: green solvents for nonaqueous biocatalysis [45], ILs in the synthesis and modification of polymers [46], chemical and biochemical transformations in ILs [21], ILs in chemical analysis [47], ILs solvent properties and organic reactivity [19], metal-containing ILs and ILs crystals based on imidazolium moiety [48], Pd-benzothiazol-2-ylidene complex in ILs [49], practical considerations associated with voltammetric studies in RTILs [50], sonochemistry and sonoluminescence in ILs, molten salts, and concentrated electrolyte solutions [51], use of ILs as "green" solvents for extractions [52], are ILs kosmotropic or chaotropic [53], application of chromatographic and electrophoretic methods for the analysis of imidazolium and pyridinium cations as used in ILs [54], analytical applications of room-temperature ILs [55], catalysis in ILs [56], dissolution of cellulose with ILs and its application [57], electrophilic reactions of aromatic and heteroaromatic compounds in ILs [58], energetic nitrogen-rich salts and ILs [59], enzyme-catalyzed reactions in ILs [60], functionalized imidazolium salts for task-specific ILs and their applications [61], ILs: an environmentally friendly media for nucleophilic substitution reactions [62], ILs as solvents for catalyzed oxidations of organic compounds [63], physical properties of ILs: database and evaluation [64],

review of ILs with fluorine-containing anions [65], supported IL phase catalysis [66], a review of ILs toward supercritical fluid applications [67], applications of ILs in carbohydrate chemistry [68], asymmetric synthesis in ILs [69], biocatalysis in nonconventional media [70], Brønsted acids in ILs [71], catalysis in ILs [24], design of sustainable chemical products – the example of ILs [72], homogeneous catalysis in ILs [73], enantioselective catalysis in ILs [74], ionic green solvents from renewable resources [6], IL thermo: a free-access web database for thermo-dynamic properties of ILs [75], ILs in separations technique [76], lanthanides and actinides in ILs [77], magnetic resonance spectroscopy in ILs [78], novel process options for the application of zeolites in supercritical fluids and ILs [79], reactiv-ity of ILs [80], self-assembled structures and chemical reactions in RTILs [81], surface chemistry of RTILs [82], transition metal-catalyzed reactions in noncon-ventional media [83], the path ahead for ILs [84], the phosphorus aspects of green chemistry [85], toxicity of ILs [86], utility of ILs in analytical separations [87], a review of ILs in chromatographic and electromigration techniques [88], advances in chiral ILs derived from natural amino acids [89], applications of chiral ILs [25], applications of ILs in the chemical industry [90], applications of ILs in elec-trochemical sensors [91], benzene alkylation with long-chain olefins catalyzed by ILs [92], biotransformations and organocatalysis with ILs [93], catalysts with ionic tag and their use in ILs [94], chemistry in heterocyclic ammonium fluorohy-drogenate room-temperature IL [95], dissolution and functional modification of cellulose in ILs [96], electrochemical reactions in ILs [97], hydroformylation in RTILs: catalyst and process developments [98], ILs in heterocyclic synthesis [27], ILs and CE combination [99], ILs as amphiphile self-assembly media [26], mac-romolecules in ILs: progress, challenges, and opportunities [100], mutual solubil-ity of hydrophobic ILs and water in liquid–liquid two-phase systems for analytical chemistry [101], predictive molecular thermodynamic models for liquid solvents [102], olefin metathesis in ILs [103], protic ILs: properties and applications [104], palladium-catalyzed reactions in ILs [105], recent advances in the synthesis and application of chiral ILs [106], recent developments on chiral ILs: design, synthe-sis, and applications [107], self-organization of imidazolium ILs in aqueous solu-tion [108], understanding ILs at the molecular level [109], advanced applications of ILs in polymer science [110], application of ILs in high-performance reversed-phase chromatography [10], designing imidazole-based ILs and IL monomers for emerging technologies [111], electrochemical behavior of aluminum in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF$_4$]) IL electrolytes for capacitor applications [112], halogenation of organic compounds in ILs [113], ILs as advanced lubricant fluids [114], IL lubricants: designed chemistry for engineering applications [115], ILs as electrolytes for Li-ion batteries [116], ILs as solvents for polymerization processes [117], ILs in tribology [118], ILs used in and ana-lyzed by capillary and microchip electrophoresis [119], ILs and their derivatives in polymer science and engineering [120], promotion of atom transfer radical polymerization and ring-opening metathesis polymerization in ILs [121], the design of polymeric ILs for the preparation of functional materials [122], assessing the greenness of some typical laboratory IL preparations [123], biodegradation

studies of ILs [124], extraction of organic compounds with RTILs [125], ILs in analytical chemistry [126], ILs and catalysis [127], ILs for CO_2 capture [128], methods for stabilizing and activating enzymes in ILs [129], microwave-assisted synthesis using ILs [130], recent advances of enzymatic reactions in ILs [131], recent applications of ILs in separation technology [132], task-specific ILs [133], the Heck reaction in ILs [134], the roles of ILs in sorptive microextraction techniques [135] and toward advanced ILs, and polar, enzyme-friendly solvents for biocatalysis [136].

1.2   History of Ionic Liquids (ILs)

Although Osteryoung, Wilkes, Hussey, and Seddon are pioneers in the field of ILs, the first report on room-temperature molten salt was published by Welton in 1914 [28]. He reported the physical properties of ethylammonium nitrate ([$C_2H_5NH_3$] NO_3), which is formed by the reaction of ethylamine with concentrated nitric acid and has a melting point of 12°C. Later on, by mixing and warming 1-ethylpyridinium chloride with aluminum chloride ($AlCl_3$), Hurley and Weir prepared another molten salt [137]. With quaternization of the heterocycle and forming mixtures with $AlCl_3$, Osteryoung revolutionized this field and reported new salts in 1978. Consequently, the effect of changing the cation was investigated by Hussey and Wilkes, and the dialkylimidazolium-based ILs were discovered [111]. The ILs based on $AlCl_3$ can be considered as the first generation of ILs, but the advancement in their use was restricted due to hygroscopic nature. Thus, they were not found suitable for open-air applications. However, the second generation of ILs as named air and water stable ILs were synthesized and attracted auxiliary attention in the use of ILs in different fields. Wilkes and Zaworotko [138] reported the synthesis of water- and air-stable dialkylimidazolium ILs. They revealed that upon anion exchange with more hydrolytically stable anions such as BF_4^-, PF_6^-, NO_3^-, SO_4^{-2} or acetate, the resulting ILs could be prepared and safely stored outside of an inert atmosphere as they are water insensitive. As regards the synthesis and applications of air-stable ILs, [BMIm][BF_4] and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]) were the first. After that, the magnitude of air- and water-stable ILs has started to increase quickly [139]. Then ILs based on more hydrophobic anions such as tri-fluoromethanesulfonate ($CF_3SO_3^-$), bis-(trifluoromethanesulfonyl)imide [Tf_2N]$^-$, and tris-(trifluoromethanesulfonyl)methide [$(CF_3SO_2)_3C^-$] were reported [140]. This development led to the birth of the modern day ILs. Rogers focuses on the synthesis and characterization of environmentally friendly ILs as green solvents and found that cellulose could be dissolved in 1-butyl-3-methyl imidazole chloride ([BMIm]Cl), which opened a new way for the development of a class of cellulose solvent systems. Many papers dealing with the applications of ILs as solvents for synthesis and catalysis have been published by Welton. He focused his study on interaction of ILs with solute species and tried to replace environmentally damaging solvents with more benign alternatives [28]. Preparation and
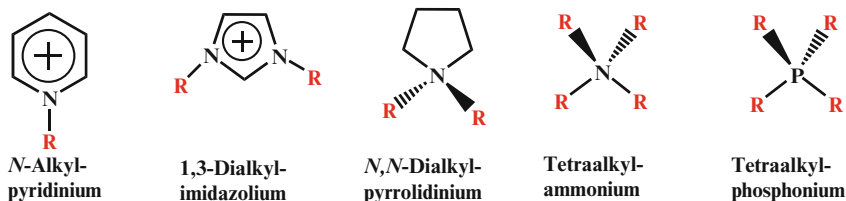
characterization of ILs for use in the biphasic catalysis were reported by Wasserscheid and Welton [141]. Jessop et al. indicated that functional groups can be incorporated in IL and make them to behave not only as a reaction medium but also as a reagent or catalyst in some reactions or processes. This group of ILs was named as "task-specific ILs." Addition of pressurized carbon dioxide into an organic mixture transforms it into an IL, generating a safer solvent in situ. Releasing of the pressure reverses the phenomenon, and the IL is retransformed into the original mixture, thus removing completely the solvent and eliminating tedious purification and extraction steps [142].

1.3   Structure of Ionic Liquids (ILs)

Similar to all salts, ILs are made up of separate cationic and anionic species, but unlike common salts, ILs have a low tendency to crystallize due to their bulky and asymmetrical cation structure. The nearly infinite combinations of suitable cations and anions lead to the possibility of tailoring the IL properties, with the anion responsible for such qualities as air and water stability and the cation responsible for melting temperature and organic solubility. They are also known as "designer solvents" since they give the opportunity to tune their specific properties for a particular need. The researchers can design a specific IL by choosing negatively charged small anions like $[Tf_2N]^-$, PF_6^-, or PF_4^- and positively charged large cations of alkylimidazolium, alkylpyridinium, alkylpyrrolidinium, alkylphosphonium, or alkylmorpholinium. These specific ILs may be utilized to dissolve a particular chemical or to extract a certain material from a solution. The fine-tuning of the structure provides tailor-designed properties to satisfy the specific application requirements. Although these particular cations and anions and their various combinations have already been studied extensively for their potential applications in numerous chemical and physical processes, every year more and more cations and anions forming liquid salts at room temperature are reported [54, 143–145]. Plechkova and Seddon estimated that there may be in excess of 10^6 possible ILs if all currently known IL cations and anions were to be paired and as many as 10^{18} if all ternary systems were to be investigated [90]. Their structures play a key role in several interesting and useful ways because their unique properties that departs from those of conventional solvents. Their coulombic nature imposes a degree of order on the short-range scale, and their amphiphilic combination of polar and nonpolar components leads to different types of correlations on longer scales [146].

The structure of cation–cation and anion–anion peaks and valleys in the pair distribution is diametrically out of phase with the cation–anion pair distribution [147]. The overall properties of ILs result from the composite properties of the cations and anions and include those that are superacidic, basic, hydrophilic, water miscible, water immiscible, and hydrophobic. The structures of most normally used cations and some possible anion are represented in Fig. 1.1.

Most Commonly Used Cations:

| *N*-Alkyl-pyridinium | 1,3-Dialkyl-imidazolium | *N,N*-Dialkyl-pyrrolidinium | Tetraalkyl-ammonium | Tetraalkyl-phosphonium |

R: Methyl, Ethyl, Butyl, Hexyl, Octyl, Decyl

Most Commonly Used Anions:

Water Immiscible → Water Miscible

$[PF_6^-]$ $[BF_3^-]$ $[CH_3CO_2^-]$

$[N(SO_2CF_3)_2^-]$ $[CF_3SO_2^-]$ $[CH_3SO_2^-]$

$[BR_4^-]$ $[NO_3^-], [Cl^-]$
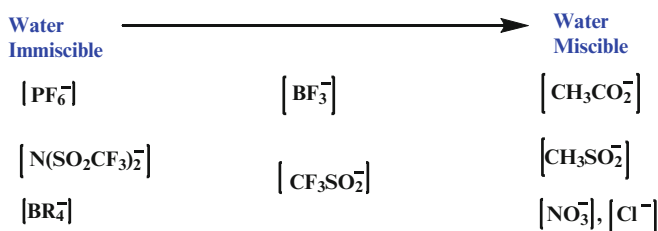
Fig. 1.1 Most commonly used cation structures and possible anion types

1.3.1 Cations

The cation of IL is usually a bulk organic structure with low symmetry which gives salts having low melting points even though dibutyl, dioctyl, dinonyl, and didecylimidazolium hexafluorophosphates are liquid at room temperature [148]. The majority of ILs are based on imidazolium, pyridinium, ammonium, phosphonium, sulfonium, thiazolium, pyrazolium, and oxazolium cations. The research mainly focuses on RTILs composed of asymmetric *N,N*-dialkylimidazolium cations associated with a variety of anions. The melting points of the most ILs are indecisive. For that reason, by examining the properties of a series of imidazolium-cation-based ILs, it has been concluded that as the size and asymmetry of the cation increases, the melting point decreases. Further, an increase in the branching on the alkyl chain increases the melting point.

ILs with specific functional groups on the cation have been prepared by different groups. For example, ILs bearing a fluorous tail have been synthesized to facilitate the emulsification of perfluorocarbons in ILs. These ILs perform as surfactants and appear to self-aggregate within imidazolium ILs [149]. A free amine group or a urea or thiourea has been inserted to capture H_2S or CO_2 or heavy metals, respectively [150]. Moreover, ether and alcohol functional groups have been attached to imidazolium cations to promote the solubility of inorganic salts. The presence of these extra potential complexing groups makes these ILs suitable for specific applications [11, 151, 152].

1.3.2 Anions

Since the nature of anion has a great effect on the properties of IL, there are major differences between ILs with different anions. The introduction of different anions results in an increasing number of alternative ILs with various properties [153]. The physical and chemical properties of the ILs can be determined by different ion pairs. IL with 1-n-butyl-3-methylimidazolium cation and PF_6^- anion is immiscible with water, whereas IL with same cation and BF_4^- anion is water soluble. This example represents the "designer solvent" property of ILs. By changing the anion, the hydrophobicity, viscosity, density, and solvation of the IL system may be changed [67].

On the basis of the anion, ILs may be divided into four groups: (a) systems based on $AlCl_3$ and organic salts such as [BMIm]Cl; (b) systems based on anions like PF_6^-, BF_4^-, and SbF_6^-; (c) systems based on anions such as $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$, $[Tf_2N]^-$, and similar; and (d) systems based on anions such as alkylsulfates and alkylsulfonates [19, 154, 155]. The first group represents the ILs of "first generation," whose Lewis acidity can be varied by the relative amounts of organic salt/$AlCl_3$. With a molar excess of $AlCl_3$, these ILs are Lewis acidic; with an excess of organic salt, they are Lewis basic; and Lewis neutral liquids contain equimolar amounts of organic salt and $AlCl_3$. These ILs are, however, extremely hygroscopic, and handling is possible only under a dry atmosphere. The systems mentioned in (b) are nearly neutral and air stable, although they have the drawback of reacting exothermically with strong Lewis acids, such as $AlCl_3$, and with water [141]. ILs based on anions mentioned in (c) are much more stable toward such reactions and are generally characterized by low melting points, low viscosities, and high conductivities. Structural studies of organic $[Tf_2N]^-$ salts have shown only weak coulombic interactions between $[Tf_2N]^-$ and weak Lewis acids, attributable to delocalization of the negative charge within the S–N–S core [156, 157].

Probably, the metal enhances the contribution of the resonance structure bearing the negative charge on the nitrogen atom. Lately, the synthesis of numerous ILs based on the bis(methanesulfonyl)amide ($[Ms_2N]^-$) anion has provided new insights into the effect of anion fluorination on the properties of ILs. The substitution of $[Tf_2N]^-$ anion with $[Ms_2N]^-$ induces a significant increase in hydrogen bonding, which determines a significant rise in the glass transition temperature with concurrent increase in viscosity, which in turn produces a drop in conductivity [158].

ILs bearing perfluorinated anions are expensive (in particular, those having $[Tf_2N]^-$ as counter anion), and the presence of fluorine makes the disposal of spent ILs more complicated. For these reasons, research on new ILs bearing inert low-coordinating and nonfluorinated anions represents a field of intense investigation in the chemistry of ILs. Among the possible alternatives recently proposed are the ILs having as carboranes and orthoborates counter anions [4]. ILs based on anions mentioned in (d) may conquer at least some of the above-mentioned problems. These anions are relatively cheap, do not contain fluorine atoms, and

often the corresponding ILs can be easily prepared under ambient conditions by reaction of organic bases with dialkyl sulfates or alkyl sulfonate esters. Moreover, these new ILs are characterized by a wide electrochemical window and air stability [153].

1.4 Synthesis of Ionic Liquids (ILs)

The growing attention in ILs, especially in the light of their current common commercial applicability, has resulted in further progresses in their synthesis and purification. Above all, this has required a shift toward improving the standard of synthetic procedures to ensure consistency in the quality of the materials. Furthermore, in order to improve the chances of large-scale commercial applications, the efficiency of synthetic procedures, IL toxicity, and biodegradation have all become important topics [141]. Notably, the inherent synthetic flexibility afforded by pairing different cations with any of a growing number of anions provides the possibility for "fine-tuning" certain IL solvent properties to the particular task at hand.

There are three basic methods to synthesize ILs: metathesis reactions, acid–base neutralization, and direct combination. Many alkylammonium halides are commercially available which can be organized simply by the metathesis reaction of the appropriate halogenoalkane and amine. Pyridinium and imidazolium halides are also synthesized by metathesis reaction. On the other hand, monoalkylammonium nitrate salts are best prepared by the neutralization of aqueous solutions of the amine with nitric acid. After neutralization reactions, ILs are processed under vacuum to remove the excess water [28]. Tetraalkylammonium sulfonates are also prepared by mixing sufonic acid and tetraalkylammonium hydroxide [159]. In order to obtain pure IL, products are dissolved in an organic solvent such as acetonitrile and treated with activated carbon, and the organic solvent is removed under vacuum. The final method for the synthesis of ILs is the direct combination of halide salt with a metal halide. Halogenoaluminate and chlorocuprate ILs are prepared by this method. The synthesis methods of ILs have been given in numerous articles [89, 138, 160, 161].

The protonation of suitable starting materials (generally amines and phosphines) still represents the simplest method for the formation of such materials, but unfortunately, it is restricted to the small range of useful salts. The possibility of decomposition via deprotonation has adversely affected the use of such salts. Probably, the most widely used salt of this type is pyridinium hydrochloride as evident from literature reviewed by Pagni [162].

The majority of ILs are formed from cations that have not been obtained by protonation of a nucleophile. A summary of the applications and properties of ILs may be found in a number of review articles [12, 19, 41, 163]. The synthesis of ILs can generally be divided into two steps: the formation of the desired cation, and anion exchange to form the desired product. In some cases, only the first step is required, as with the formation of $[C_2H_5NH_3]NO_3$. In many cases, the desired cation

is commercially available at reasonable cost, most commonly as a halide salt, thus requiring only the anion exchange reaction. The steps involved in the synthesis of ILs are described below.

1.4.1 Quaternization Reactions

The formation of the cations may be carried out either via protonation with a free acid or by quaternization of an amine, phosphine, or sulfide, most commonly using a haloalkane or dialkylsulfates. The protonation reaction, as used in the formation of salts such as $[C_2H_5NH_3]NO_3$, involves the addition of nitric acid to a cooled aqueous solution of ethylamine [164]. The excess amine is removed along with the water by heating to 60°C in vacuum. The same general process may be employed for the preparation of all salts of this type, but when amines of higher molecular weight are employed, there is clearly a risk of contamination by residual amine. A similar method has been reported for the formation of low-melting, liquid crystalline, long-alkyl-chain-substituted 1-alkylimidazolium chloride, nitrate, and tetrafluoroborate salts [165]. At this point, a slight excess of acid could be employed as the products are generally crystalline at room temperature.

The quaternization of amines and phosphines with haloalkanes has been known for many years. In general, the reaction may be carried out using chloroalkanes, bromoalkanes, and iodoalkanes, with the milder reaction conditions in the order $Cl \rightarrow Br \rightarrow I$, as is expected for nucleophilic substitution reactions. Fluoride salts cannot be formed in this manner.

In theory, the quaternization reactions are extremely simple: the amine (or phosphine) is mixed with the desired alkylating agent, and the mixture is then stirred and heated. The following section refers to the quaternization of 1-alkylimidazoles, as these are the most common starting materials. The common methods are similar, but for other amines such as pyridine, isoquinoline, 1,8-diazabicyclo[5.4.0]-7-undecene, 1-methylpyrrolidine, and trialkylamines, as well as for phosphines, it is not popular [140, 166–168]. The reaction temperature and time varied according to the nature of the alkylating agent employed, chloroalkanes being the least reactive and iodoalkanes the most. The reactivity of the haloalkanes generally decreases with increasing alkyl chain length. Several different protocols have been reported, but most researchers use a simple round-bottomed flask/reflux condenser experimental setup for the quaternization reaction. If possible, the reaction should be carried out under dinitrogen or some other inert gas in order to exclude water and oxygen during the quaternization reactions [141].

1.4.2 Anion-Exchange Reactions

The anion-exchange reactions of ILs can be alienated into two distinct categories: direct reaction of halide salts with Lewis acids and the formation of ILs via anion metathesis.

1.4.2.1   Lewis-Acid-Based Ionic Liquids (ILs)

The formation of ILs by the reaction of halide salts with Lewis acids (most notably $AlCl_3$) dominated in the infancy of this area of chemistry. The great breakthrough came in 1951 with the report by Hurley and Weir on the formation of a salt that was liquid at room temperature based on the combination of 1-butylpyridinium with $AlCl_3$ in the relative molar proportions 1:2 [169]. The technology of room-temperature chloroaluminate melts based on 1-alkylpyridinium and 1-alkyl-3-methyl-imidazolium [RMIm]⁺ cations has been developed in recent years [170]. In general, the reaction of a quaternary halide salt Q^+X^- with a Lewis acid MX_n results in the formation of more than one anion species, depending on the relative proportions of Q^+X^- and MX_n. The chloroaluminates are not the only ILs prepared in this manner. Other Lewis acids employed include $AlEtCl_2$, BCl_3, $CuCl$, $SnCl_2$, and $FeCl_3$. In most cases, the preparative methods employed for all of these salts are similar to those indicated for $AlCl_3$-based ILs [141].

The most common method for the formation of such liquids is simple mixing of the Lewis acid and the halide salt, with the IL forming on contact of the two materials. The reaction is generally quite exothermic, which means that care should be taken when adding one reagent to the other. Although the salts are relatively thermally stable, the buildup of excess local heat can result in decomposition and discoloration of the IL. This may be prohibited either by cooling the mixing vessel or by adding one component to the other in small portions to allow the heat to dissipate. Considering the water-sensitive nature of most of the starting materials, the reaction be carried out in a drybox and the ILs should preferably be stored in a drybox until use [141].

1.4.2.2   Anion Metathesis

The first report on the development of air- and water-stable ILs was reported by Wilkes and Zaworotko [138] which was based on 1,3-dialkylmethylimidazolium cations. The preparation involved a metathesis reaction between 1-ethyl-3 methylimidazolium iodate [EMIm]I and a range of silver salts ($Ag[NO_3]$, $Ag[NO_2]$, $Ag[BF_4]$, $Ag[CH_3CO_2]$, and $Ag_2[SO_4]$) in methanol or aqueous methanol solution. The very low solubility of silver iodide in these solvents allowed its separation simply by filtration, and removal of the reaction solvent allowed isolation of the ILs in high yield and purity. This method remains the most efficient for the synthesis of water-miscible ILs, but is obviously limited by the relatively high cost of silver salts, not to mention the large quantities of solid by-product produced [141]. The first report on a water-insoluble IL appeared 2 years later, with the preparation of $[EMIm][PF_6]$ from the reaction of [EMIm]Cl and HPF_6 in aqueous solution [171]. Though the protocols reported in the above two papers were sound, subsequent authors suggested refinements in the methods employed. Most of the [EMIm]⁺-based salts are solid at room temperature, facilitating purification via recrystallization. In many applications, however, a product is required that is liquid at room temperature. Therefore, it is useful to employ cations with 1-alkyl substituents of chain length 4 or greater, which

results in a considerable lowering in melting point. The main goal of all anion exchange reactions is the formation of the desired IL uncontaminated with unwanted cations or anions, a task that is easier for water immiscible ILs.

It should be noted, however, that low-melting salts based on symmetrical onioum cations have been prepared using anion-exchange reactions for many years. For instance, the preparation of tetrahexylammonium benzoate (a liquid at 25°C) from tetrahexylammonium iodide, silver oxide, and benzoic acid was reported in 1967. The same authors also commented on an alternative approach involving the use of an ion-exchange resin for the conversion of the iodide salt to hydroxide, but concluded that this approach was less desirable. Low-melting salts based on cations such as tetrabutylphosphonium [172] and trimethylsulfonium [173] have also been produced using very similar synthetic methods.

As the preparation of water-immiscible ILs is considerably more straightforward than the preparation of their water-soluble analogues, these methods will be considered first. The water solubility of the ILs is highly dependent on the nature of both the anion and cation present and, in general, will decrease with increasing organic character of the cation. The most common approach for the preparation of water-immiscible ILs is first to prepare an aqueous solution of a halide salt of the desired cation. The cation exchange is then carried out using either the free acid of the appropriate anion or a metal or ammonium salt. Where available, the free acid is probably to be favored, as it leaves only HCl, HBr, or HI as the by-product which can be easily removed from the final product by washing with water. It is recommended that these reactions are carried out with cooling of the halide salt in an ice bath, as the addition of a strong acid to an aqueous solution is often exothermic [141]. In cases where the free acid is inconvenient to use, however, alkali metal or ammonium salts may be substituted without major problems. It may also be preferable to avoid using the free acid in systems where the presence of traces of acid may cause problems. A number of authors have outlined broadly similar methods for the preparation of $[PF_6]^-$ and $[Tf_2N]^-$ salts that may be adapted for most purposes [170, 174]. When free acids are used, the washing should be continued until the aqueous residues are neutral, as traces of acid can cause decomposition of the IL. The most common approach is to perform the exchange in aqueous solution using either the free acid of the appropriate anion, the ammonium salt, or an alkali metal salt. When using this approach, it is significant that the desired IL can be isolated without excess contamination from unwanted halide-containing by-products. A reasonable compromise has been suggested by Welton et al. for the preparation of $[BMIm][BF_4]$ [175]. In this method, which could in principle be adapted to many other water-miscible systems, the IL is formed by metathesis between $[BMIm]Cl$ and HBF_4 in aqueous solution. The product is extracted into CH_2Cl_2, and the organic phase is then washed with successive small portions of deionized water until the pH of washings reach to neutral value. Although the water wash can result in a lowering of the yield, the aqueous wash solutions may ultimately be collected together, the water removed, and the crude salt added to the next batch of IL prepared. In this manner, the amount of product loss is minimized, and the purity of the IL prepared appears to be reasonable for most applications.

Alternatively, the metathesis reaction may be carried out entirely in an organic solvent such as CH_2Cl_2, as described by Cammarata et al. [176], or acetone, as

described by Fuller et al. [177]. In both of these systems, the starting materials are not fully soluble in the reaction solvent, so the reaction is carried out in a suspension. In the case of the CH_2Cl_2 process, the reaction was carried out by stirring the 1-alkyl-3-methylimidazolium halide salt with the desired metal salt at room temperature for 24 h. Although the halide by-products have limited solubility in CH_2Cl_2, they are reasonably soluble in the IL/CH_2Cl_2 mixture. Thus, when this method is employed, it is important that the CH_2Cl_2 extracts are washed with water to minimize the halide content of the final product. This approach clearly results in a lowering of the yield of the final product. Therefore, care must be taken that the volume of water used to carry out the washing is low. Lowering the temperature of the water to near 0°C can also reduce the amount of IL loss. The final product can be purified by stirring with activated charcoal followed by passing through an alumina column, as described in the previous paragraph. This process was reported to give final yields in the region of 70–80% and was used to prepare ILs containing a wide variety of anions ($[PF_6]^-$, $[SbF_6]^-$, $[BF_4]^-$, $[ClO_4]^-$, $[CF_3SO_3]^-$, $[NO_3]^-$, and $[CF_3CO_2]^-$). In the case of the acetone route, [EMIm]Cl was stirred with $[NH_4][BF_4]$ or $[NH_4][CF_3SO_3]$ at room temperature for 72 h. In this case, all starting materials were only slightly soluble in the reaction solvent. The insoluble $[NH_4]Cl$ by-product was removed by filtration. No water wash was carried out, but trace organic impurities were removed by stirring the acetone solution with neutral alumina for 2 h after removal of the metal halide salts by filtration. The salts were finally dried by heating at 120°C for several hours, after which they were analyzed for purity by electrochemical methods, giving quoted purities of at least 99.95% [177].

1.5   Properties of Ionic Liquids (ILs)

ILs with many interesting properties are currently enjoying popularity among chemists. Overall, generalizing and reporting their properties is not easy because some of the properties such as electrochemical window, long-term thermal stability, polarity, and volatility have been the subject of debate. This happens due to better understanding and adequate characterization of ILs with improved quantification of their impurities which are well known to affect the thermophysical properties of them [127]. Water solubility of an IL can be tuned by changing the R group on the cation component. In addition, by the choice of the anion, chemical and physical properties can be changed significantly. The generic properties of ILs have been described in literature [146] and can be easily found in a database.

1.5.1   Melting Point

The key criterion for the evaluation of an IL is its melting point. Although ILs have been defined to have melting points below 100°C and most of them are liquid at room temperature, data must be considered with caution. The melting point of many ILs

may be uncertain because they undergo considerable supercooling, the temperature of the phase change which can differ considerably depending on whether the sample is heated or cooled, and also because of the potential presence of impurities [127]. There is a significant relationship between the structure and chemical composition of an IL and its melting point. This physical property can be adjusted through variations on the cation and/or anion, and both cations and anions contribute to the low meting points of ILs. The increase in anion size leads to a decrease in melting point. For instance, the melting points of 1-ethyl-3-methylimidazolium-type ILs with different anions, such as [BF$_4$]$^-$ and [Tf$_2$N]$^-$, are 15°C and −3°C, respectively [178]. Comparison of the melting points of different chlorine salts illustrates the influence of the cation clearly. High melting points are characteristic for alkali metal chloride, whereas chloride with suitable organic cation melts at temperatures below 150°C. In the literature, the following features are discussed for the cations of low-melting salt: low symmetry, weak intermolecular interaction such as avoidance of hydrogen bonding, and a good distribution of charge in the cation. For IL prepared by reaction of halide [cation]$^+$X$^-$ with a Lewis acid MX$_\lambda$, the molar ratio of two reactants influences the melting point [29]. Further, an increase in the branching on the alkyl chain increases the melting point.

1.5.2 Volatility

In addition to the favorable physical and chemical properties of ILs, an important property of ILs that stimulates interest in using them in the context of so-called green chemistry is their essentially zero vapor pressure even at elevated temperatures. ILs are indeed nonvolatile in that sense that at near ambient temperatures their vapor pressure is negligible. For typical ILs, normal boiling temperatures (T$_b$), which correlate with their vapor pressure at one atmosphere, cannot be experimentally determined as ILs decomposes at a lower temperature. It has nevertheless been reported that ILs can be distilled at 200–300°C but under significantly reduced pressure and at very low distillation rate (<0.01 g h^{-1}). Vapor pressure of ILs remains, however, negligible at near ambient conditions; thus, for all practical purposes, they may be considered as nonvolatile solvents [35]. On the whole, the negligible volatility of these ILs denotes that air pollution by gaseous release is not a concern. ILs are considered as nonvolatile and, consequently, nonflammable at ambient and higher temperatures. However, the potential release of IL vapors (or decomposition products) must be considered when ILs are used at elevated temperatures.

1.5.3 Thermal Stability

Thermogravimetric analysis indicates high thermal stability for many ILs, generally >350°C. For example, ILs [EMIm][BF$_4$], [BMIm][BF$_4$], and 1,2-dimethyl-3-propy-limidazolium bis(trifluorosulfonyl)imide are stable up to temperatures of 445°C,

423°C, and 457°C, respectively [127]. Such high temperatures are only tolerated by most liquids for a short time. For example, after 10 h, even at temperatures as low as 200°C, [RMIm][PF$_6$] and 1-decyl-3-methylimidazolium triflate show an appreciable mass loss [179]. The ILs with low thermal stability are [EMIm][X], where X = [Tf$_2$N]$^-$, [M$_S$N]$^-$, and Br$^-$ [68]. Phosphonium ILs with [Tf$_2$N]$^-$ or [N(CN)$_2$]$^-$ anions decompose completely to volatile products in a single step. The degradation products indicate that Hofmann elimination process and/or dealkylation reactions occurred. Conversely, ILs based on nitrogen cations do not decompose completely [127]. The start of thermal decomposition is furthermore similar for the different cations but appears to decrease as the anion hydrophilicity increases. It has been suggested that the stability dependency on the anion is in the order [PF$_6$]$^-$ > [Tf$_2$N]$^-$ [BF$_4$]$^-$ > halides. An increase in cation size, at least from 1-butyl to 1-octyl, does not offer large effect [19].

1.5.4 Viscosity

The viscosity of many ILs is relatively high compared to conventional solvents, one to three orders of magnitude higher. The viscosity is determined by van der Waals forces, hydrogen bonding, and electrostatic forces. The ability of fluorinated anions such as BF^{-4} and PF^{-6} to the formation of hydrogen bonding results in the formation of viscous ILs [178]. The presence of AlCl$_4^-$ and Al$_2$Cl$_7^-$ in acidic mixture leads to formation of weaker hydrogen bond and much lower viscosity. The transition from triflate ion to n-C$_4$F$_9$SO$_3$ and from the triflouroacetate ion to the n-C$_3$F$_7$COO$^-$ ion shows an obvious increase in viscosity. In fact, stronger van der Waals forces lead to increase in the energy required for molecular motion. The case of n-C$_4$F$_9$SO$_3$ and n-C$_3$F$_7$COO$^-$ ions results in a higher viscosity of IL. Comparison of the viscosity of the [BMIm]CF$_3$SO$_3$ with [BMIm][Tf$_2$N] reveals a lower viscosity despite stronger van der Waals interaction. In this case, the almost complete suppression of hydrogen bond is responsible for expected increase viscosity [29]. For a variety of ILs, viscosity has been reported in the range 10–500 mPa s^{-1} at room temperature. The viscosity of ILs can affect transport properties such as diffusion and plays a major role in stirring, mixing, and pumping operations.

1.5.5 Density

ILs are generally denser than either organic solvents or water, with typical density values ranging from 1 to 1.6 g cm^{-3}. Their densities were found to decrease with increase in the length of the alkyl chain in the cation. For example, for ILs composed of substituted imidazolium cations and CF$_3$SO$_3^-$ anion, the density decreases from 1.39 g cm^{-3} for [EMIm] 1 to 1.33 g cm^{-3} for [E$_2$Im], to 1.29 g cm^{-3} for [BMIm], and to 1.27 g cm^{-3} for [BEIm] 1.22. Density of an IL depends on the type

of cation and anion. The density of comparable ILs decreased as the bulkiness of the organic cation increase. The order of increasing density for ILs composed of a single cation is $[CH_3SO_3]^- \approx [BF_4]^- < [CF_3CO_2]^- < [CF_3SO_3]^- < [C_3F_7CO_2]^- < [(CF_3SO_2)_2N]^-$ [178]. The molar mass of the anion significantly affects the overall density of ILs. The $[Ms_2N]^-$ species have lower densities than the $[Tf_2N]^-$ salts, in agreement with the fact that the molecular volume of the anion is similar but the mass of the fluorine is greater. In the case of orthoborates, with the exception of bis(salicylato)borate, the densities of the ILs having the [BMIm] cation decrease with increase in anion volume. This order is also followed in ILs, those having $[Tf_2N]^-$, $[TfO]^-$, or $[BF_4]^-$ as anion. This behavior has been attributed to the fact that packing becomes more compact as the alternating positive and negative species are more even in size [19]. Density measurement of IL with triflate or trifluoroacetete ions confirms the more general trend. Furthermore, a certain density range is established by the choice of anion, within which a fine adjustment is possible by careful choice of cation [29].

1.5.6   Polarity

To classify the solvents, the polarity is one of the most important properties for characterizing the solvent effect in chemical reactions. In IUPAC document, polarity is defined as "the sum of all possible, nonspecific interactions between the solute ions and molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute" [67]. The subject of IL polarity has been addressed by a variety of methodologies. As an example, the property of solvents to stabilize a charge is usually determined from the absorption maximum of a solvatochromic dye. By this measurement, the polarity, archetypical [BMIm][BF_4], is in the range of the lower alcohols. A solvatochromic test for the coordination strength (nucleophilicity) of the anion, in contrast, indicates that the often used $[PF_6]$ and $[Tf_2N]$ anions are much less nucleophilic than the lower alcohols [32]. Although solvatochromic dyes can be used to determine empirical polarity parameters, these parameters are probably not truly independent on the probe molecule used. The difficulty in the case of ILs is to find a suitable soluble probe which measures the polarity parameters as independently as possible from other influences of the solvent [127]. Measurement of keto-enol equilibria is another approach to solvent polarity, which is dependent on the polarity of the medium. Based on this methodology, the polarity of [BMIm][BF_4], [BMIm][PF_6], or [BMIm][NTf_2] was higher than methanol or acetonitrile. Microwave dielectric spectroscopy measurements can also be used for the remaining measurement of dielectric constants of a number of ILs. By this measurement, the polarities of [BMIm][BF_4] and [BMIm][PF_6] are in the range of a medium-chain alcohol, such as 1-hexanol or 1-octanol, with marked contributions from the anion as well the cation [32].

1.5.7 Conductivity and Electrochemical Window

An attractive aspect of ILs is their conductivity by virtue of which they are very useful solvents and electrolytes in electrochemical reactions. Based on the fact that ILs are composed solely of ions, it would be expected that ILs have high conductivities. However, the conductivity of any solution depends not only on the number of charge carriers but also on the viscosity, density, ion size, anionic charge delocalization, aggregations, and ionic mobility. The large size of ions of ILs reduces the ion mobility which, in turn, leads to lower conductivities. Furthermore, ion pair formation and/or ion aggregation leads to reduced conductivity. The conductivity of ILs is inversely linked to their viscosity. Hence, ILs of higher viscosity exhibit lower conductivity [178]. In general, higher conductivities are found for imidazolium-based ILs in comparison with the ammonium-based ILs. Strong ion-pair associations have been invoked in the case of $[Tf_2N]^-$-based ILs, to understand their lower conductivity in comparison with $[BF_4]^-$-based ILs. ILs exhibit broad range of conductivities spanning from 0.1 to 20 mS cm^{-1} [127]. ILs by their electrochemical window play a key role in electrodeposition of metals and semiconductors. By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. Because of its low electrochemical window, the electrodeposition of elements and compounds in water is restricted. On the contrary, ILs have significantly larger electrochemical windows, found in the range 4.5–5 V, which is similar to or slightly larger than that found in conventional organic solvents, but larger than that of aqueous electrolytes. In general, the wide electrochemical windows of ILs have opened the door for electrodeposit ion of metals and semiconductors at room temperature which were formerly obtained only from high temperature molten salts. For example, Al, Mg, Si, Ge, and rare earth elements can be obtained from RTILs. The thermal stability of ILs allows to electrodeposit Ta, Nb, V, Se, and presumably many other ones at elevated temperature [19, 178, 180].

1.5.8 Toxicity

The main reason for believing ILs to be nontoxic results from their nonvolatile properties, which makes them potential green substitutes for conventional volatile organic solvents. Unfortunately, this green image is misplaced and has recently aroused the awareness of chemists, especially those working in the area of green chemistry. It is easy to found that some of cations and anions for preparing IL are hazardous, so it is wrong to assume that the risk hazards of these precursors will fade away following their conversion into ILs. On the other hand, incorporating different functional groups makes it complicated to investigate the toxicity of ILs because of the potential virulence of the incorporated functionalities. Though ILs may help in reducing the risk of air pollution, their release to aquatic environments could cause severe water

contamination because of their potential toxicity and inaccessible biodegradability. Because of the relative stability features of ILs, their accumulation in the environment becomes feasible, if they are applied in operational use. Thus, the fundamentals of IL biodegradability turn out to be an important issue for the reduction of ignition and landfill-waste risks. Therefore, various efforts to produce biodegradable and biorenewable ILs that can be obtained through modification of natural sources have been undertaken [67, 127].

1.5.9   Air and Moisture Stability

Many of ILs are both air and moisture stable. Conversely, most imidazolium and ammonium salts are hydrophilic, and if they are used in open vessels, hydration will certainly take place. The hydrophobicity of an IL increases with increasing length of the alkyl chain. Despite their widespread usage, ILs containing PF_6^- and BF_4^- have been reported to decompose in the presence of water, giving off HF. Wasserscheid et al. [181] pointed out that ILs containing halogen anions generally show poor stability in water and also produce toxic and corrosive species such as HF or HCl. Therefore, they suggest the use of halogen-free and relatively hydrolysis-stable anions such as octylsulfate compounds. The interaction between water and ILs and their degree of hydroscopic character are strongly dependent on anions. The amount of absorbed water is highest in the BF_4^- and lowest in PF_6^- [182]. However, $[Tf_2N]^-$ is much more stable in the presence of water as well as having the advantage of an increased hydrophobic character. ILs immiscible with water tend to absorb water from the atmosphere. The infrared studies demonstrated that the water molecules absorbed from the air are mostly present in the free state and bonded via H-bonding with the PF_6^- and BF_4^- anions. The presence of water may have dramatic effect on the reactivity of ILs. Since water is present in all ILs, they are usually utilized after a moderate drying process. The newly synthesized ILs are more stable than the old halogenoaluminate systems. Certain ILs incorporating 1-3-dialkylimidazolium cations are generally more resistant than traditional solvents under harsh process conditions, such as those occurring in oxidation, photolysis, and radiation processes [167].

1.5.10   Cost and Biodegradability

Cost and biodegradability have also been major concerns, and new families of ILs derived from renewable feedstock or from "low-cost" starting materials have been described. These "Bio-ILs" are entirely composed of biomaterials [183]. An example to be cited is the development of the "deep eutectic mixtures" liquid systems based on choline chloride [184] for which the qualification of "ILs" is still the subject of controversies. Choline can be used as alternative cation in combination with suitable anion to generate ILs. The biodegradable properties of these ILs have been reported [185].

Very recently, it was shown that the introduction of an ester group into long alkyl chains leads to reduce toxicity and improve ecotoxicity of ILs. Further, incorporation of ether groups into the side chain improves the biodegradability of imidazolium-based ILs, while the introduction of the biodegradable octylsulfate anion has a further beneficial effect. Recent work on pyridinium-based ILs demonstrated how the heteroaromatic cationic core can be modified to produce biodegradable ILs. As with the imidazolium examples, the inclusion of an ester group in the cation side chain led to improved biodegradability. High levels of biodegradability have also been reported in cases where environmentally benign anions such as saccharinate and acesulfamate are included. Several ammonium ILs based on choline have been introduced which are biodegradable and can be readily prepared [124].

1.6   Solvent Properties and Solvent Effects

Solvents are commonly characterized by macroscopic physical constants such as vapor pressure, surface tension, boiling point, density, relative permittivity ε_r (dielectric constants), cohesive pressure, and refractive index. Many chemical reactions are carried out in homogenous media using conventional solvents. However, it is difficult to find solvents in which covalent organic compounds and ionic inorganic reagents as well as catalysts are adequately soluble to achieve a homogeneous reaction mixture. Furthermore, upon the completion of reaction, chemical products have to be removed from the solvent. There are some methods to recover a product from a solvent. For example, water-soluble compounds may be extracted in water and the distillation may be used for chemicals with high vapor pressures [67]. Alternatively, for chemicals with low vapor pressures, distillation must be performed at low pressures. In addition to this, there are some chemicals that can decompose as a result of heating, such as pharmaceutical compounds. Additionally, isolation of the product(s) requires a fairly lengthy work-up procedure. ILs seem to be potentially good solvents for many chemical reactions in cases where distillation is not practical, or water insoluble or thermally sensitive products are the components of a chemical reaction. They are immiscible with most of the organic solvents, thus they provide a nonaqueous, polar alternative for two-phase systems [67]. Moreover, ILs which are not miscible with water can be used as immiscible polar phases with water. Although all other conventional solvents evaporate to the atmosphere, ILs do not evaporate and their nonvolatility gives an opportunity to utilize them in high vacuum systems. The negligible volatility is the basic property which characterizes them as green solvents. Considering as potential solvents, ILs can easily replace other conventional organic solvents which are used in large quantities in chemical processing industries to eliminate major environmental problems. Many studies have been directed to the characterization of ILs and their "bulk" physicochemical properties [56].

The dielectric constant is an important parameter of solvent that reflects its molecular symmetry. It is worth to emphasize that the favorable methods for

determining dielectric constants fail in case of ILs because of their high electrical conductivities. However, it could be measured for a series of imidazolium-based ILs using microwave dielectric spectroscopy. ILs can be classified as moderately polar solvents. Dielectric constant (ε) values are found in the range of 8.8–15.2, decreasing with increasing the length of the alkyl chain on the imidazolium cation. However, the variation is small compared to the wide range variation in (ε) values of molecular solvents (2–180) [85, 186]. The dielectric constants were found to depend mainly on the nature of the ILs anions. However, the abundant different interactions acting together in ILs make them very complex so that it is not surprising that a single physical parameter such as the dielectric constant is incapable of adequately modeling the solvent–solute interactions. This parameter has often failed in correlating solvent effects qualitatively and quantitatively. An example is given by the solvent effect study on nucleophilic reactions in ILs compared to molecular solvents where Hugues–Ingold viewpoint using dielectric constant as a measure of solvent polarity proved to be insufficient to explain the IL system [187]. For a rational design and a better choice of ILs, better understanding of their properties is required.

1.6.1   Solute–Ionic Liquids (ILs) Interactions

The solvent properties of ILs are mainly determined by the ability of the salt to act as a hydrogen bond donor and/or acceptor and the degree of localization of the charges on the anions [28]. Charge distribution on the anions, H-bonding ability, polarity, and dispersive interactions are the main factors that influence the physical properties of ILs. For example, imidazolium-based ILs are highly ordered hydrogen-bonded solvents and they have strong effects on chemical reactions and processes [67].

Many studies have focused on the cation–anion interactions (solvent–solvent interactions) rather than ions–solute interactions (solvent–solute interactions or solvent solvation). In conventional medium, solvent–solute interactions are generally predominant, while in ILs, interactions inside the solvent are more important. The Diels–Alder reaction is an interesting example because it is a key step in many syntheses. In the case of the reaction of cyclopentadiene and methyl acrylate, the ability of the IL to act as H-bond donor (cation effect) appeared to be a key criterion to explain the enhancement of reaction rate and endoselectivity [188]. This effect has to be moderated by the H-bond acceptor ability of the IL (anion effect). ILs with strong H-bond interaction between the cation and the anion (contact pair ions) are poor solvents for Diels–Alder due to competition between the anion and the H-bond acceptor dienophile for H-bonding with the cation. It is not surprising that low yields have been reported for dialkylimidazolium bromide and trifluoroacetate ILs. This H-bonding with the substrate can be influenced by p-stacking of the imidazolium cations and H-bonding interactions between the cation and the anion of the IL [127].

Another good example of model reaction to examine the IL effect is the nucleophilic substitution reactions [127]. In molecular solvents, the Hughes–Ingold qualitative model describes the solvent effect considering the pure electrostatic interactions between ions or dipolar molecules in initial and transition states (solvent polarity). This model does not take into account the H-bond interactions and proved to be limited to describe ILs effect. Kamlet–Taft linear solvation energy relationship has also been utilized to describe ILs effect on nucleophilic reactions. The characteristic values of α, β, and π* have been collected for ILs [189]. The solvent's hydrogen donor ability (α value) appears as the dominant effect in reducing the nucleophilicity of the nucleophile and slowing the reaction rate [190]. Hard and soft natures of the nucleophile also proved to be important, the [BMIm] cation of the ILs acting as a hard "solvent" in interacting more strongly with hard anions (e.g., [Cl]$^-$) than soft ones (e.g., [CN]$^-$). Compared to molecular solvents, the nucleophilicity of halide anions (e.g., [Br]$^-$) in the S_N2 reactions of methyl-*p*-nitrobenzenesulfonate was reduced in ILs (the reaction is 15 times slower in *N*-butyl-3-methylpyridinium ([BMP])[Tf$_2$N] than in dichloromethane, and it is roughly two times slower in [BMIm][Tf$_2$N] than in [BMP][Tf$_2$N]). This can be ascribed to the existence of strong H-bond between the nucleophile (the anion, particularly the chloride) and the [BMIm] cation. This difference arises largely from the α value [127].

Another systematic study on nucleophilicity of a series of anions on the substitution reaction of methanesulfonic group was conducted in different ILs and compared with that obtained in organic solvents (PhCl, DMSO, and MeOH). The results emphasize the predominant role of water for hydrophilic anions ([Cl]$^-$ and [PhCO$_2$]$^-$). In this case, the interaction of the anion with the imidazolium has a lower effect. These results confirm that water molecules create H-bond with the imidazolium cation replacing the cation–anion interactions present in the ILs [191]. Higher reactivity is also observed in C(2)-protected imidazolium-based ILs. The case of charged electrophiles within the framework of S_N2 reactions is also of fundamental interest since many catalytic centers carry positive charges. The reaction of chloride ion with an ionic electrophile (sulfonium associated with [Tf$_2$N]$^-$ or [TfO]$^-$) was studied in several molecular solvents and ILs. The nucleophilic substitution reaction does not take place in either strong dissociating molecular water solvents or in methanol. In nondissociating solvent, the reaction is supposed to occur via a solvated ion pairs. The behavior of this reaction in ILs is different from that in molecular solvents; the kinetic experiments in ILs are in favor of reaction via dissociated ions. The results show that ILs can be considered as superdissociating solvents, this effect arising from the fact that ILs are at the same time liquid and ionic. The reaction mechanism would proceed through a true S_N2 reaction of free solvated ions rather than with α ion-pair mechanism seen in molecular solvents [192]. Based on these model reactions, we can assume that the interactions between ILs and different species are of diverse nature and complex which significantly modify their reactivity. The interactions of ILs with selected solutes will be discussed below.

1.6.1.1   Interaction of Ionic Liquids (ILs) with Water

The hydrophilic/hydrophobic behavior is significant for the solvation properties of ILs as it is essential to dissolve reactants, but it is also relevant for the recovery of products by solvent extraction. In addition, the water content of ILs can affect the rates and selectivity of reactions. One potential problem with ILs is the possible pathway into the environment through wastewater. The effect of water in modifying IL properties has been a central focus of recent interest [127]. This factor has been illustrated by the examination of water solvation at low and high concentrations. IR [176] and dielectric constant [193] studies have revealed that water is molecularly dispersed in 1-alkyl-3-methyl imidazolium-based ILs ([$H_2O < 2$ M]) at low concentrations. When the water concentration is increased, water molecules aggregate and form a well-defined water hydrogen-bonds network [193]. It is found that the local organization between ions precludes any specific interactions between water and the proton of the imidazolium cation. Water would be doubly hydrogen-bonded with two anions, in symmetric 2:1 [Anion–H–O–H–Anion] structures. PCl_3 and $POCl_3$ show unexpectedly high hydrolytic stability in wet ILs. For example, in the [Tf_2N]⁻-based ILs, PCl_3 was soluble at concentrations up to 0.20 M, and in [BMP][Tf_2N], it was found to be hydrolytically stable for weeks, even when stirred in air. The ability of even wet ILs to stabilize hydrolytically unstable solutes may be understood by considering the interaction of water with IL. The nucleophilicity of water and therefore its hydrolysis tendency can be reduced due to its interaction with IL anions. In hydrophilic ILs, the higher water content results in higher rate of hydrolysis [194]. Interestingly, ILs have been used to improve the solubility of hydrophobic compounds in water. For example, the solubility of acetophenone in aqueous solution can be increased by a factor of 10 by addition of [BMIm][BF_4], which can be important for application in biocatalysis. This phenomenon can be explained by the ability of ILs to form small aggregates which are solvent dependent [195].

1.6.1.2   Interaction of Ionic Liquids (ILs) with Acid and Base

The importance of ILs as solvents to perform acid–base reactions has been recently realized. A straightforward way to create and modulate the acidity is to add a Brønsted acid into the IL. Therefore a new level of acidity can be found either by varying the acid concentration in the IL or by changing the nature of the IL [161]. A lot of acid-catalyzed reactions have been reported in ILs, but only few studies have been devoted to the quantification of the acidity level of the proton in these media. However, as the acidity of protons is mainly determined by their solvation state, the properties of protons will depend strongly on the nature of the IL and the nature and concentration of the acid. Relative estimation of the proton acidity level has been reported using the determination of the Hammett acidity functions, by UV–vis spectroscopy [160]. For the same content

of added strong acid, the anion of ILs plays a fundamental role; the acidity levels are in the order: $[PF_6]^- > [BF_4]^- > [Tf_2N]^- > [TfO]^-$, thus implying that the solvating power (or basicity) of the anions follows the reverse order. The presence of basic impurities in the ILs can also have a dramatic effect. Even if absolute acidities cannot be determined with this method, global acidity must be higher than that observed in water [161].

1.6.1.3 Interaction of Ionic Liquids (ILs) with Aromatic Hydrocarbon

Aromatic hydrocarbons show unusual high solubility in ILs as compared to aliphatic compounds. This extent of solubility decreases with an increase in the molecular weight of the hydrocarbon, but the differences of solubilities of *o*-, *m*-, and *p*-xylenes are not significant [161]. Previous studies show that imidazolium-based ILs can form liquid clathrates in the presence of aromatic hydrocarbons [160]. Dialkylimidazolium cations are able to form specific and oriented interactions with arenes. For instance, in the salt crystal $[BMIm][PF_6]$, 0.5 benzene, a three-dimensional network has been observed with H-bonds between anion and cation. This results in the formation of channels containing the benzene molecules. Short interactions between methyl hydrogen of the cation and aromatic hydrogen are present [196]. Interactions between *p*-aromatic systems and inorganic cations (Li^+, Na^+, K^+, or Ag^+) or organic cations (ammonium) are already well known as the "p-cation interaction," important in biochemistry, and experimentally evidenced [197]. A detailed study conducted with the aid of NMR and molecular simulation shows difference in interaction of toluene with the ILs due to the substitution of the C(2) of the imidazolium cation. In the case of the [BMIm] cation, toluene is located closer to the methyl group at the end of the butyl chain, whereas in the case of [BMMiI] cation, toluene was closer to C(2)-Me of the imidazolium. The H-bonding association between $[BMI]^+$ and $[Tf_2N]^-$ is too strong to be cleaved by toluene. In the case of C(2)-Me cation, the less strongly bonded IL network renders possible the penetration and interaction of toluene [197].

1.6.1.4 Interaction with Chiral Substrates

Some chiral ILs have been designed and synthesized. They have already been applied in different fields such as asymmetric synthesis, stereoselective polymerization, chiral chromatography, liquid crystals, chiral resolution, and NMR shift reagents [20, 106, 107]. Chiral solvents have been reported in asymmetric syntheses. In the Baylis–Hillman reaction of benzaldehyde and methyl acrylate in the presence of bases, chiral ILs demonstrate their ability in the transfer of chirality, even if the enantiomeric excesses (ee) are still moderate. The presence of an alcoholic functional group on the *N*-alkyl-*N* methylephedrinium is primordial and acts as a fixing point of the chiral IL on the reactants. It is assumed that the OH is connected

with a carbonyl group of the substrate (from either benzaldehyde or methyl acrylate) via H-bonding [127, 198]. However, with *N*-methylephedrine, very low ee are obtained which also indicate that the ammonium group plays a crucial role in the chirality induction. Even if not directly demonstrated, it seems that the key of effective asymmetric induction is the existence of both strong intermolecular interactions, like electrostatic attraction and hydrogen bonding, between ionic solvents and intermediates or transition states of the diastereoselective reaction step. The need of H-bonding in the transfer of chirality has also been confirmed in the case of borate-based chiral IL bearing maleic acid functions. In this latter case, by incorporating the acidic center into the chiral anion of the solvent, the IL offers the possibility of establishing a bifunctional interaction, which allows monofunctional achiral nucleophiles to be used as catalysts [199–201].

1.7   Conclusions

VOCs are often difficult to separate from the desired reaction products, problematic to recycle, and challenging to dispose of without encountering extra costs and/or adversely affecting the environment. Therefore, the interest of ILs as "green" solvents resides in their extremely low vapor pressure and high thermal stability, which offer advantages such as ease of containment, product recovery, and recycling ability. Due to their attractive properties, ILs are being used for a wide variety of applications. Current research indicates that replacing an organic solvent with an IL can bring about remarkable improvements in well-known chemical processes. ILs are being used extensively as solvent systems for chemical and polymerization reactions in addition to their use as biocatalysis. ILs have also been increasingly used in separation science, gas chromatography, liquid chromatography, and capillary electrophoresis. ILs have also found uses in liquid–liquid extraction, immunoassays, lubricants, and embalming/tissue preservation. Additionally, the change of the cation and/or anion component of the IL provides a way to adjust all properties, allowing the potential to fine-tune an IL for specific tasks. These features allow ILs to be used as potential alternative solvents to VOCs in a wide variety of industrial chemical applications.

It is hoped that successful commercialization of technologies utilizing these neoteric solvents will be a key driver for their continued development and integration into the chemical industry. Large-scale industrial manufacture of the ILs themselves is clearly a necessary precursor for this process. We also believe that due to the extensive variety in ILs formation and applications, they will play an important role in future environmentally friendly science and technology.

References

1. Gemmell V (1990) VOC reduction. Solvent cleaning and paint stripping. Trans Soc Auto Eng 99:64–76
2. Matlack A (2003) Some recent trends and problems in green chemistry. Green Chem 5:7–12
3. Xie YY (2005) Organic reactions in ionic liquids: ionic liquid-accelerated one-pot synthesis of 2-arylimidazo[1,2-a]pyrimidines. Synthetic Commun 35:1741–1746
4. Wu W, Li W, Han B et al (2005) A green and effective method to synthesize ionic liquids: supercritical CO_2 route. Green Chem 7:701–704
5. Guerrero-Sanchez C, Lobert M, Hoogenboom R et al (2007) Microwave-assisted homogeneous polymerizations in water-soluble ionic liquids: an alternative and green approach for polymer synthesis. Macromol Rapid Commun 28:456–464
6. Imperato G, Konig B, Chiappe C (2007) Ionic green solvents from renewable resources. Eur J Org Chem 2007: 1049–1058
7. Laszlo JA, Compton DL (2001) α-Chymotrypsin catalysis in imidazolium-based ionic liquids. Biotechnol Bioeng 75:181–186
8. Renner R (2001) Ionic liquids: an industrial cleanup solution. Environ Sci Technol 35: 410–413
9. Visser AE, Holbrey JD, Rogers RD (2001) Hydrophobic ionic liquids incorporating N-alkylisoquinolinium cations and their utilization in liquid–liquid separations. Chem Commun 2484–2485
10. Wang Y, Tian M, Bi W, Row KH (2009) Application of ionic liquids in high performance reversed-phase chromatography. Int J Mol Sci 10:2591–2610
11. Huang JF, Luo H, Liang C et al (2008) Advanced liquid membranes based on novel ionic liquids for selective separation of olefin/paraffin via olefin-facilitated transport. Ind Eng Chem Res 47:881–888
12. Dupont J, de Souza RF, Suarez PAZ (2002) Ionic liquid (molten salt) phase organometallic catalysis. Chem Rev 102:3667–3692
13. Fang MH, Wang LS (2007) Hydrolysis and partial recycling of a chloroaluminate ionic liquid. Int J Mol Sci 8:470–477
14. Mallakpour S, Dinari M (2007) Molten salt as a green reaction medium: synthesis of polyureas containing 4-phenylurazole moiety in the main chain in the presence of tetrabutylammonium bromide as an ionic liquid. e-Polymer no. 035:1–8
15. Wasserscheid P (2006) Volatile times for ionic liquids. Nature 439:797
16. Earle MJ, Seddon KR (2000) Ionic liquids. Green solvents for the future. Pure Appl Chem 72:1391–1398
17. Fraga-Dubreuil J, Famelart MH, Bazureau JP (2002) Ecofriendly fast synthesis of hydrophilic poly(ethyleneglycol)-ionic liquid matrices for liquid-phase organic synthesis. Org Process Res Dev 6:374–378
18. Binnemans K (2005) Ionic liquid crystals. Chem Rev 105:4148–4204
19. Chiappe C, Pieraccini D (2005) Ionic liquids: solvent properties and organic reactivity. J Phys Org Chem 18:275–297
20. Ding J, Armstrong DW (2005) Chiral ionic liquids: synthesis and applications. Chirality 17: 281–292
21. Jain N, Kumar A, Chauhan S et al (2005) Chemical and biochemical transformations in ionic liquids. Tetrahedron 61:1015–1060
22. Liao L, Liu L, Zhang C, Gong S (2006) Microwave-assisted ring-opening polymerization of ε-caprolactone in the presence of ionic liquid. Macromol Rapid Commun 27:2060–2064
23. Liao L, Zhang C, Gong S (2007) Microwave-assisted ring-opening polymerization of trimethylene carbonate in the presence of ionic liquid. J Polym Sci Polym Chem 45:5857–5863
24. Parvulescu VI, Hardacre C (2007) Catalysis in ionic liquids. Chem Rev 107:2615–2665
25. Bica K, Gaertner P (2008) Applications of chiral ionic liquids. Eur J Org Chem 2008: 3235–3250

26. Greavesa TL, Drummond CJ (2008) Ionic liquids as amphiphile self-assembly media. Chem Soc Rev 37:1709–1726
27. Martins MAP, Frizzo CP, Moreira DN et al (2008) Ionic liquids in heterocyclic synthesis. Chem Rev 108:2015–2050
28. Welton T (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev 99:2071–2083
29. Wasserscheid P, Keim W (2000) Ionic liquid – New solutions for transition metal catalysis. Angew Chem Int Ed 39:3772–3789
30. Wilkes JS (2002) A short history of ionic liquids – from molten salts to neoteric solvents. Green Chem 4:73–80
31. Marsh KN, Deer A et al (2002) Room temperature ionic liquids as replacements for conventional solvents. Korean J Chem Eng 19:357–362
32. van Rantwijk F, Lau MR, Sheldon RA (2003) Is there a new biosynthetic pathway for lung surfactant phosphatidylcholine? Trends Biotechnol 21:131–133
33. Baudequin C, Baudoux J, Levillain J et al (2003) Ionic liquids and chirality: opportunities and challenges. Tetrahedron Asymmetry 14:3081–3093
34. van Rantwijk F, Sheldon RA (2007) Biocatalysis in ionic liquids. Chem Rev 107:2757–2785
35. Kubisa P (2004) Application of ionic liquids as solvents for polymerization processes. Prog Polym Sci 29:3–12
36. Poole CF (2004) Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. J Chromatogr A 1037:49–82
37. Shi F, Gu Y, Zhang Q, Deng Y (2004) Development of ionic liquids as green reaction media and catalysts. Catal Surv Asia 8:179–176
38. Antonietti M, Kuang D, Smarsly B et al (2004) Ionic liquids for the convenient synthesis of functional nanoparticles and other inorganic nanostructures. Angew Chem Int Ed 43:4988–4992
39. Welton T (2004) Ionic liquids in catalysis. Coord Chem Rev 248:2459–2477
40. Buzzeo MC, Evans RG, Compton RG (2004) Non-haloaluminate room-temperature ionic liquids in electrochemistry. Chem Phys Chem 5:1106–1120
41. Davis JH (2004) Task-specific ionic liquids. Chem Lett 33:1072–1077
42. Liu J, Jonsson JA, Jiang G (2005) Application of ionic liquids in analytical chemistry. Trends Anal Chem 24:20–27
43. Garcia MT, Gathergood N, Scammells PJ (2005) Biodegradable ionic liquids part II. Effect of the anion and toxicology. Green Chem 7:9–14
44. Zhao H (2005) Effect of ions and other compatible solutes on enzyme activity, and its implication for biocatalysis using ionic liquids. J Mol Catal B: Enzym 37:16–25
45. Yang Z, Pan WB (2005) Ionic liquids: green solvents for nonaqueous biocatalysis. Enzyme Microb Technol 37:19–28
46. Kubisa P (2005) Ionic liquids in the synthesis and modification of polymers. J Polym Sci A: Polym Chem 43:4675–4683
47. Koel M (2005) Ionic liquids in chemical analysis. Crit Rev Anal Chem 35:177–192
48. Lin IJB, Vasam CS (2005) Metal-containing ionic liquids and ionic liquid crystals based on imidazolium moiety. J Organomet Chem 690:3498–3512
49. Calo V, Nacci A, Monopoli A (2005) Pd-benzothiazol-2-ylidene complex in ionic liquids: efficient catalyst for carbon–carbon coupling reactions. J Organomet Chem 690:5458–5466
50. Zhang J, Bond AM (2005) Practical considerations associated with voltammetric studies in room temperature ionic liquids. Analyst 130:1132–1147
51. Flannigan DJ, Hopkins SD, Suslick KS (2005) Sonochemistry and sonoluminescence in ionic liquids, molten salts, and concentrated electrolyte solutions. J Organomet Chem 690:3513–3517
52. Zhao H, Xia S, Ma P (2005) Use of ionic liquids as 'green' solvents for extractions. J Chem Technol Biotechnol 80:1089–1096
53. Zhao H (2006) Are ionic liquids kosmotropic or chaotropic. J Chem Technol Biotechnol 81:877–891

54. Stepnowski P (2006) Application of chromatographic and electrophoretic methods for the analysis of imidazolium and pyridinium cations as used in ionic liquids. Int J Mol Sci 7: 497–509

55. Pandey S (2006) Analytical applications of room-temperature ionic liquids: a review of recent efforts. Anal Chim Acta 556:38–45

56. Zhang ZC (2006) Catalysis in ionic liquids. Adv Catal 49:153–237

57. Zhu S, Wu Y, Chen Q et al (2006) Dissolution of cellulose with ionic liquids and its application: a mini-review. Green Chem 8:325–327

58. Borodkin GI, Shubin VG (2006) Electrophilic reactions of aromatic and heteroaromatic compounds in ionic liquids. Russian J Org Chem 42:1745–1770

59. Singh RP, Verma RD, Meshri DT et al (2006) Energetic nitrogen-rich salts and ionic liquids. Angew Chem Int Ed 45:3584–3601

60. Moon YH, Lee SM, Ha SH et al (2006) Enzyme-catalyzed reactions in ionic liquids. Korean J Chem Eng 23:247–263

61. Lee SG (2006) Functionalized imidazolium salts for task-specific ionic liquids and their applications. Chem Commun 1049–1063

62. Jorapur YR, Chi DY (2006) Ionic liquids: an environmentally friendly media for nucleophilic substitution reactions. Bull Korean Chem Soc 27:345–354

63. Muzart J (2006) Ionic liquids as solvents for catalyzed oxidations of organic compounds. Adv Synth Catal 348:275–295

64. Zhang S, Sun N, He X (2006) Physical properties of ionic liquids: database and evaluation. J Phys Chem Ref Data 35:1475–1517

65. Xue H, Verma R, Shreeve JM (2006) Review of ionic liquids with fluorine-containing anions. J Fluorine Chem 127:159–176

66. Riisager A, Fehrmann R, Haumann M et al (2006) Supported ionic liquid phase (SILP) catalysis: an innovative concept for homogeneous catalysis in continuous fixed-bed reactors. Eur J Inorg Chem 2006: 695–706

67. Keskin S, Kayrak-Talay D, Akman U et al (2007) A review of ionic liquids towards supercritical fluid applications. J Supercrit Fluids 43:150–180

68. El Seoud OA, Koschella A, Fidale LC et al (2007) Applications of ionic liquids in carbohydrate chemistry: a window of opportunities. Biomacromolecules 8:2629–2647

69. Paczal A, Kotschy A (2007) Asymmetric synthesis in ionic liquids. Monatsh Chem 138: 1115–1123

70. Canton S, Hanefeld U, Basso A (2007) Biocatalysis in non-conventional media-ionic liquids, supercritical fluids and the gas phase. Green Chem 9:954–971

71. Johnson KE, Pagni RM, Bartmess J (2007) Brønsted acids in ionic liquids: fundamentals, organic reactions, and comparisons. Monatsh Chem 138:1077–1101

72. Ranke J, Stolte S, Stormann R et al (2007) Design of sustainable chemical products. Chem Rev 107:2183–2206

73. Giernoth R (2007) Homogeneous catalysis in ionic liquids. Top Curr Chem 276:1–23

74. Durand J, Teuma E, Gomez M (2007) Ionic liquids as a medium for enantioselective catalysis. Compt Rendus Chim 10:152–157

75. Dong Q, Muzny CD, Kazakov A (2007) IL thermo: a free-access web database for thermodynamic properties of ionic liquids. J Chem Eng Data 52:1151–1159

76. Berthod A, Ruiz-Angel MJ, Carda-Broch S (2008) Ionic liquids in separation techniques. J Chromatogr A 1184:6–18

77. Bankmann D, Giernoth R (2007) Magnetic resonance spectroscopy in ionic liquids. Prog Nucl Magn Reson Spectrosc 51:63–90

78. Binnemans K (2007) Lanthanides and actinides in ionic liquids. Chem Rev 107:2592–2614

79. Glaser R (2007) Novel process options for the application of zeolites in supercritical fluids and ionic liquids. Chem Eng Tech 30:557–568

80. Chowdhury S, Mohan RS, Scott JL (2007) Reactivity of ionic liquids. Tetrahedron 63: 2363–2389

81. Hao J, Zemb T (2007) Self-assembled structures and chemical reactions in room-temperature ionic liquids. Curr Opin Colloid Interface Sci 12:129–137

82. Aliaga C, Santos CS, Baldelli S (2007) Surface chemistry of room-temperature ionic liquids. Phys Chem Chem Phys 9:3683–3700
83. Liu S, Xiao J (2007) Toward green catalytic synthesis-transition metal-catalyzed reactions in non-conventional media. J Mol Catal A Chem 270:1–43
84. Joglekar HG, Rahman I, Kulkarni BD (2007) The path ahead for ionic liquids. Chem Eng Tech 30:819–828
85. Keglevich G, Baan Z, Hermecz I et al (2007) The phosphorus aspects of green chemistry. Curr Org Chem 11:107–126
86. Zhao D, Liao Y, Zhang Z (2007) Toxicity of ionic liquids. Clean 35:42–48
87. Shamsi SA, Danielson ND (2007) Utility of ionic liquids in analytical separations. J Sep Sci 30:1729–1750
88. Buszewski B, Studzinska S (2007) A review of ionic liquids in chromatographic and electro-migration techniques. Chromatographia 68:1–10
89. Chen X, Li X, Hua A, Wang F (2008) Advances in chiral ionic liquids derived from natural amino acids. Tetrahedron Asymmetry 19:1–14
90. Plechkova NV, Seddon KR (2008) Applications of ionic liquids in the chemical industry. Chem Soc Rev 37:123–150
91. Wei D, Ivaska A (2008) Applications of ionic liquids in electrochemical sensors. Anal Chim Acta 607:126–135
92. Congzhen Q, Yonghong C, Quanhui G (2008) Benzene alkylation with long chain olefins catalyzed by ionic liquids. Front Chem Eng China 2:346–352
93. de Maria PD (2008) "Nonsolvent" applications of ionic liquids in biotransformations and organocatalysis. Angew Chem Int Ed 47:6960–6968
94. Sebesta R, Kmentova I, Toma S (2008) Catalysts with ionic tag and their use in ionic liquids. Green Chem 10:484–496
95. Tsuda T, Hagiwara R (2008) Chemistry in heterocyclic ammonium fluorohydrogenate room-temperature ionic liquid. J Fluorine Chem 129:4–13
96. Feng L, Chen Z (2008) Research progress on dissolution and functional modification of cellulose in ionic liquids. J Mol Liq 142:1–5
97. Hapiot P, Lagrost C (2008) Electrochemical reactivity in room-temperature ionic liquids. Chem Rev 108:2238–2264
98. Haumann M, Riisager A (2008) Hydroformylation in room temperature ionic liquids (RTILs): catalyst and process developments. Chem Rev 108:1474–1497
99. Lopez-Pastor M, Simonet BM, Lendl B et al (2008) Ionic liquids and CE combination. Electrophoresis 29:94–107
100. Ueki T, Watanabe M (2008) Macromolecules in ionic liquids: progress, challenges, and opportunities. Macromolecules 41:3739–3749
101. Kakiuchi T (2008) Mutual solubility of hydrophobic ionic liquids and water in liquid–liquid two-phase systems for analytical chemistry. Anal Sci 24:1221–1230
102. Lei Z, Chen B, Li C, Hui L (2008) Predictive molecular thermodynamic models for liquid solvents, solid salts, polymers, and ionic liquids. Chem Rev 108:1419–1455
103. Sledz P, Mauduit M, Grela K (2008) Olefin metathesis in ionic liquids. Chem Soc Rev 37:2433–2442
104. Greaves TL, Drummond CJ (2008) Protic ionic liquids: properties and applications. Chem Rev 108:206–237
105. Singh R, Sharma M, Mamgain R et al (2008) Ionic liquids: a versatile medium for palladium-catalyzed reactions. J Braz Chem Soc 19:357–379
106. Winkel A, Reddy PVG, Wilhelm R (2008) Recent advances in the synthesis and application of chiral ionic liquids. Synthesis 7:999–1016
107. Patil ML, Sasai H (2008) Recent developments on chiral ionic liquids: design, synthesis, and applications. Chem Rec 8:98–108
108. Luczak J, Hupka J, Thöming J et al (2008) Self-organization of imidazolium ionic liquids in aqueous solution. Colloids Surf A: Physicochem Eng Aspects 329:125–133

109. Weingrtner H (2008) Understanding ionic liquids at the molecular level: facts, problems, and controversies. Angew Chem Int Ed 47:654–670

110. Lu J, Yan J (2009) Advanced applications of ionic liquids in polymer science. Prog Polym Sci 34:431–448

111. Green MD, Long TE (2009) Designing imidazole-based ionic liquids and ionic liquid monomers for emerging technologies. J Macromol Sci R, Part C: Polym Rev 49:291–314

112. Trombetta F, de Souza MO, de Souza RF et al (2009) Electrochemical behavior of aluminum in 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid electrolytes for capacitor applications. J Appl Electrochem 39:2315–2321

113. Pavlinac J, Zupan M, Laali KK et al (2009) Halogenation of organic compounds in ionic liquids. Tetrahedron 65:5625–5662

114. Bermudez MD, Jimenez AE, Sanes J et al (2009) Ionic liquids as advanced lubricant fluids. Molecules 14:2888–2908

115. Zhou F, Liang Y, Liu W (2009) Ionic liquid lubricants: designed chemistry for engineering applications. Chem Soc Rev 38:2590–2599

116. Lewandowski A, Swiderska-Mocek A (2009) Ionic liquids as electrolytes for Li-ion batteries-an overview of electrochemical studies. J Power Sources 194:601–609

117. Kubisa P (2009) Ionic liquids as solvents for polymerization processes-progress and challenges. Prog Polym Sci 34:1333–1347

118. Minami I (2009) Ionic liquids in tribology. Molecules 14:2286–2305

119. Xu Y, Wang E (2009) Ionic liquids used in and analyzed by capillary and microchip electrophoresis. J Chromatogr A 1216:4817–4823

120. Gibson HW (2009) Ionic liquids and their derivatives in polymer science and engineering. J Macromol Sci R, Part C: Polym Rev 49:289–290

121. Xie M, Han H, Ding L et al (2009) Promotion of atom transfer radical polymerization and ring-opening metathesis polymerization in ionic liquids. J Macromol Sci R, Part C: Polym Rev 49:315–338

122. Green O, Grubjesic S, Lee S et al (2009) The design of polymeric ionic liquids for the preparation of functional materials. J Macromol Sci R, Part C: Polym Rev 49:339–360

123. Deetlefs M, Seddon KR (2010) Assessing the greenness of some typical laboratory ionic liquid. Green Chem 12:17–30

124. Coleman D, Gathergood N (2010) Biodegradation studies of ionic liquids. Chem Soc Rev 39:600–637

125. Poole CF, Poole SK (2010) Extraction of organic compounds with room temperature ionic liquids. J Chromatogr A 1217:2268–2286

126. Sun P, Armstrong DW (2010) Ionic liquids in analytical chemistry. Anal Chim Acta 661:1–16

127. Olivier-Bourbigou H, Magna L, Morvan D (2010) Ionic liquids and catalysis. Appl Catal A: Gen 373:1–56

128. Hasibur-Rahman M, Siaj M, Larachi F (2010) Ionic liquids for CO_2 capture. Chem Eng Process 49:313–322

129. Zhao H (2010) Methods for stabilizing and activating enzymes in ionic liquids. J Chem Technol Biotechnol 85:891–907

130. Martinez-Palou R (2010) Microwave-assisted synthesis using ionic liquids. Mol Divers 14:3–25

131. Moniruzzaman M, Nakashima K, Kamiya N et al (2010) Recent advances of enzymatic reactions in ionic liquids. Biochem Eng J 48:295–314

132. Han D, Row KH (2010) Recent applications of ionic liquids in separation technology. Molecules 15:2405–2426

133. Giernoth R (2010) Task-specific ionic liquids. Angew Chem Int Ed 49:2834–2839

134. Bellina F, Chiappe C (2010) The heck reaction in ionic liquids. Molecules 15:2211–2245

135. Aguilera-Herrador E, Lucena R, Cardenas S et al (2010) The roles of ionic liquids in sorptive microextraction techniques. Trends Anal Chem 29:602–616

136. Gorke J, Srienc F, Kazlauskas R (2010) Toward advanced ionic liquids. Polar, enzyme-friendly solvents for biocatalysis. Biotechnol Bioprocess Eng 15:40–53
137. Hurley FH, Wier TP (1951) Electrodeposition of metals from fused quaternary ammonium salts. J Electrochem Soc 98:203–206
138. Wilkes JS, Zaworotko MJ (1992) Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. J Chem Soc Chem Commun 965–967
139. Dupont J (2004) On the solid, liquid and solution structural organization of imidazolium ionic liquids. J Braz Chem Soc 15:341–350
140. MacFarlane DR, Meakin P, Sun J et al (1999) Pyrrolidinium imides: a new family of molten salts and conductive plastic crystal phases. J Phys Chem B 103:4164–4170
141. Wasserscheid P, Welton T (2007) Ionic liquids in synthesis. Wiley-VCH, Weinheim
142. Jessop PG, Heldebrant DJ, Li X et al (2005) Reversible nonpolar-to-polar solvent. Nature 436:1102
143. Olah GA, Mathew T, Goeppert A et al (2005) Ionic liquid and solid HF equivalent amine-poly(hydrogen fluoride) complexes effecting efficient environmentally friendly isobutane-isobutylene alkylation. J Am Chem Soc 127:5964–5969
144. Rodrıguez O, Madeira PP, Macedo EA (2008) Gibbs free energy of transfer of a methylene group in buffer ionic liquid biphasic systems. Ind Eng Chem Res 47:5165–5168
145. Schmidt-Naake G, Woecht I, Schmalfuß A et al (2009) Free adical polymerization in ionic liquids-solvent influence of new dimension. Macromol Symp 275–276:204–218
146. Castner EW, Wishart JF (2010) Spotlight in ionic liquids. J Chem Phys 132:120901–120909
147. Tosi MP, Price DL, Saboungi ML (1993) Ordering in metal halide melts. Annu Rev Phys Chem 44:173–211
148. Dyzuba SV, Bartsch RA (2001) New room-temperature ionic liquids with C2-symmetrical imidazolium cations. Chem Commun 16:1466–1467
149. Merringan TL, Bates ED, Dorman SC et al (2000) Chem Commun 20:2051–2052
150. Visser AE, Swatloski RP, Rogers RD (2001) So you think your process is green, how do you know? Green Chem 2:1–6
151. Holbrey JD, Seddon KR, Rogers RD (1999) Clean Prod Process 1:223–236
152. Rogers RD, Seddon KR (2002) In ionic liquids: industrial applications to green chemistry, vol 818, ACS Symposium Series. American Chemical Society, Washington, DC
153. Shariati A, Peters CJ (2005) High pressure phase equilibria of systems with ionic liquids. J Supercrit Fluids 34:171–176
154. Brinchi L, Germani R, Savelli G (2003) Ionic liquids as reaction media for esterification of carboxylate sodium salts with alkyl halides. Tetrahedron Lett 44:2027–2029
155. Holbrey JD, Reichert WM, Swatloski RP et al (2002) Efficient, halide free synthesis of new low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. Green Chem 4:407–413
156. Golding JJ, MacFarlane DR, Spiccia L (1998) Weak intermolecular interactions in sulfon-amide salts: structure of 1-ethyl-2-methyl-3-benzyl imidazolium bis[(trifluoromethyl)sulfo-nyl]amide. Chem Commun 15:1593–1594
157. Polyakov OG, Ivanova SM, Gaudinski CM et al (1999) Cu(CO)2(N(SO2CF3)2). The first structurally characterized copper(I) polycarbonyl. Organometallics 18:3769–3771
158. Pringle JM, Golding J, Baranyai K et al (2003) The effect of anion fluorination in ionic liquids-physical properties of a range of bis(methanesulfonyl)amide salts. New J Chem 27:1504–1510
159. Poole SK, Shetty PH, Poole CF (1989) Chromatographic and spectroscopic studies of the solvent properties of a new series of room-temperature liquid tetraalkylammonium sulfonates. Anal Chim Acta 218:241–264
160. Holbrey JD, Reichert WM, Nieuwenhuyzen M (2003) Liquid clathrate formation in ionic liquid–aromatic mixtures. Chem Commun 476–477
161. Mirzaei YR, Twamley B, Shreeve JM (2002) Syntheses of 1-alkyl-1,2,4-triazoles and the formation of quaternary 1-alkyl-4-polyfluoroalkyl-1,2,4-triazolium salts leading to ionic liquids. J Org Chem 67:9340–9345

162. Pagni RM (1987) In: Mamantov G, Mamantov CB, Braunstein J (eds) Advances in molten salt chemistry. Elsevier, New York, pp 211–346
163. Gordon CM (2001) New developments in catalysis using ionic liquids. Appl Catal A Gen 222:101–117
164. Evans DF, Yamouchi A, Wei GJ et al (1983) Micelle size in ethylammonium nitrate as determined by classical and quasi-elastic light scattering. J Phys Chem 87:3537–3541
165. Lee CK, Huang HW, Lin IJB (2000) Simple amphiphilic liquid crystalline N-alkylimidazolium salts. A new solvent system providing a partially ordered environment. Chem Commun 1911–1912
166. Gordon CM, Holbrey JD, Kennedy AR et al (1998) Ionic liquid crystals: hexafluorophosphate salts. J Mater Chem 8:2627–1636
167. Kitazume T, Zulfiqar F, Tanaka G (2000) Molten salts as a reusable medium for the preparation of heterocyclic compounds. Green Chem 2:133–136
168. Visser AE, Swatloski RP, Reichert WM et al (2008) Ionic liquids in microemulsions. Environ Sci Technol 36:2523–2529
169. Hurley FH, Weir TP (1951) The electrodeposition of aluminum from nonaqueous solutions at room temperature. J Electrochem Soc 98:207–212
170. Huddleston JG, Willauer HD, Swatlowski RP et al (1998) Room temperature ionic liquids as novel media for 'clean' liquid–liquid extraction. Chem Commun 1765–1766
171. Fuller J, Carlin RT, DeLong HC et al (1994) Structure of 1-ethyl-3-methylimidazolium hexafluorophosphate: model for room temperature molten salts. Chem Commun 299–300
172. Pomaville RM, Poole SK, Davis LJ et al (1998) Solute–solvent interactions in tetra-n-butylphosphonium salts studied by gas chromatography. J Chromatogr 438:1–14
173. Matsumoto H, Matsuda T, Miyazaki Y (2000) Room temperature molten salts based on trialkylsulfonium cations and bis(trifluoromethylsulfonyl)imide. Chem Lett 29:1430–1431
174. Bonhote P, Dias AP, Papageorgiou N et al (1996) Hydrophobic, highly conductive ambient-temperature molten salts. Inorg Chem 35:1168–1178
175. Lancaster NL, Welton T, Young GB (2001) A study of halide nucleophilicity in ionic liquids. J Chem Soc Perkin Trans 2:2267–2270
176. Cammarata L, Kazarian SG, Salter PA et al (2001) Molecular states of water in room temperature ionic liquids. Phys Chem Chem Phys 3:5192–51200
177. Fuller J, Carlin RT (1999) Proc Electrochem Soc 98:227–230
178. Endres F, El Abedinw SZ (2006) Air and water stable ionic liquids in physical chemistry. Phys Chem Chem Phys 8:2101–2116
179. Kosmulski M, Gustafsson J, Rosenholm JB (2004) Thermochim Acta 412:47–53
180. Ohno Y (2005) Electrochemical aspects ionic liquids. John Wiley Sons Inc., New Jersey
181. Wasserscheid P, van Hal R, Bosmann A (2002) 1-n-Butyl-3-methylimidazolium ([bmim]) octylsulfate-an even 'greener' ionic liquid. Green Chem 4:400–404
182. Tran CD, Lacerda SDP, Oliveira D (2003) Absorption of water by room temperature ILs: effect of anions on concentration and state of water. Soc Appl Spectrosc 57:152–157
183. Fukaya Y, Iizuka Y, Sekikawa K et al (2007) Bio ionic liquids: room temperature ionic liquids composed wholly of biomaterials. Green Chem 9:1155–1157
184. Abbott AP, Boothby D, Capper G et al (2004) Model studies on p-hydroxybenzoate hydroxylase. J Am Chem Soc 126:127–142
185. Yu Y, Lu X, Zhou Q et al (2008) Biodegradable naphthenic acid ionic liquids: synthesis, characterization, and quantitative structure-biodegradation relationship. Chem Eur J 14:11174–11182
186. Weingartner H, Sasisanker P, Daguenet C et al (2007) The dielectric response of room-temperature ionic liquids: effect of cation variation. J Phys Chem B 111:4775–4780
187. Ranieri G, Hallett JP, Welton T (2008) Nucleophilic reactions at cationic centers in ionic liquids and molecular solvents. Ind Eng Chem Res 47:638–644
188. Aggarwal A, Lancaster NL, Sethi AR et al (2002) The role of hydrogen bonding in controlling the selectivity of Diels-Alder reactions in room-temperature ionic liquids. Green Chem 2:517–520

189. Crowhurst L, Mawdsley P, Perez-Arlandis JM (2003) Solvent-solute interactions in ionic liquids. Phys Chem Chem Phys 5:2790–2794
190. Crowhurst L, Falcone R, Lancaster NL (2006) Using Kamlet-Taft solvent descriptors to explain the reactivity of anionic nucleophiles in ionic liquids. J Org Chem 71:8847–8853
191. Betti C, Landini D, Maia A (2008) Reactivity of anionic nucleophiles in ionic liquids and molecular solvents. Tetrahedron 64:1689–1695
192. Hallett JP, Liotta CL, Ranieri G et al (2009) Charge screening in the SN2 reaction of charged electrophiles and charged nucleophiles: an ionic liquid effect. J Org Chem 74:1864–1868
193. Dimitrakis G, Villar Garcia IJ, Lester E (2008) Dielectric spectroscopy: a technique for the determination of water coordination within ionic liquids. Phys Chem Chem Phys 10: 2947–2951
194. Amigues E, Hardacre C, Keane G et al (2006) Ionic liquids-media for unique phosphorus chemistry. Chem Commun 72–74
195. Dorbritz S, Ruth W, Kragl U (2005) Investigation on aggregate formation of ionic liquids. Adv Synth Catal 347:1273–1279
196. Lachwa J, Szydlowski J, Makowska A et al (2006) Changing from an unusual high-temperature demixing to a UCST-type in mixtures of 1-alkyl-3-methylimidazolium bis{(trifluoromethyl) sulfonyl}amide and arenes. Green Chem 8:262–267
197. Ma JC, Dougherty DA (1997) The cation – π interaction. Chem Rev 97:1303–1324
198. Gutel T, Santini CC, Padua AAH et al (2009) Interaction between the π-system of toluene and the imidazolium ring of ionic liquids. J Phys Chem B 113:170–177
199. Gausepohl R, Buskens P, Kleinen J et al (2006) Highly enantioselective aza-Baylis–Hillman reaction in a chiral reaction medium. Angew Chem Int Ed 45:3689–3695
200. Baudequin C, Bregeon D, Levillain J (2005) Chiral ionic liquids, a renewal for the chemistry of chiral solvents. Tetrahedron Asymmetry 16:3921–3945
201. Ishida Y, Sasaki D, Miyauchi H et al (2004) Design and synthesis of novel imidazolium-based ionic liquids with a pseudo crown-ether moiety: diastereomeric interaction of a racemic ionic liquid with enantiopure europium complexes. Tetrahedron Lett 45:9455–9459