1

An Introduction to Ionic Liquids

1.1 Prologue

The benefits of using salts in their liquid form as electrolytes or reaction media have long been recognized. For example, Faraday developed his laws of electrolysis in the 1830s using molten metal halide salts. However, most researchers would rather avoid using solvents that require heating to hundreds of degrees. Therefore, while ‘high-temperature molten salts’ are extremely useful for certain applications, they are not in widespread use in research laboratories or industry. In contrast, ‘ionic liquids’ – and we will discuss the definition of these below – are proving to be very exciting for a very wide range of applications at more moderate temperatures. Particularly over the last decade, scientists working in many different areas of research have started to realize the special properties of ionic liquids (ILs) and to embrace the promise of these new materials. As more applications are discovered, and more families of ILs are developed, so the field continues to grow. Thousands of papers on ILs are now published every year, and, more importantly, increasing numbers of researchers are experimenting with ILs and discovering firsthand how their unique properties can help their work.

So here we are, just over 100 years since the first ‘room-temperature ionic liquid’ was discovered, at a point where these materials are now proving so promising and widely applicable that it is important for a broad range of scientists and engineers to have an appreciation of the basics of ILs. Thus, the purpose of this book is to serve as an introduction to the key concepts and applications of ILs for those venturing into this field for the first time. Hopefully, the book will also inspire further curiosity and enthusiasm for exploring these exciting and very unique materials.

Our goal in this book is to provide a thorough introduction to the field appropriate to the level of a finishing undergraduate science student or a beginning postgraduate student. Our emphasis is on illustrative examples and the background chemistry sufficient to understand the fundamentals of ILs and their applications. For further reading, we have referenced more extensive reviews where they exist. To provide background on fundamental concepts and methods that may not be readily accessible in standard textbooks, we have included Concept Toolbox items as breakout text boxes in various places throughout the chapters. This first chapter provides a broad overview of the field, the materials

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involved, their properties, and their applications, of which more details can be found later in this book.

1.2 The Definition of an Ionic Liquid

The phrase ‘ionic liquid’ was coined only relatively recently to refer to ambient-temperature liquid salts, and the definition has since been the subject of much discussion and some evolution. The most useful practical definition of an IL is

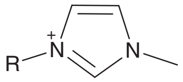
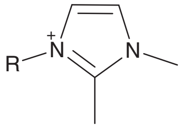
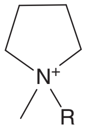
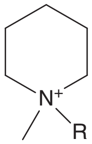
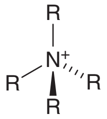
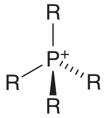
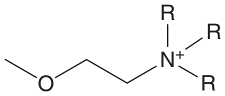
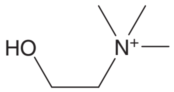
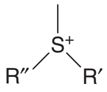
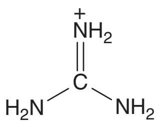
> ‘A liquid comprised entirely of ions.’

We can delve into this a little deeper. By this definition, is an IL different from a molten salt? The answer is: ‘No’ – the term ‘molten salt’ refers to the liquid phase of a crystalline salt, for example, NaCl. ‘Ionic Liquid’ covers that, but also covers a broader range of possibilities. Imagine a mixture of the two salts Na[fsi] and [C_3mpyr][NTf_2] (see Table 1.1 for an explanation of abbreviations). This mixture of salts is a liquid at room temperature and is properly called an IL by our definition. In fact an IL could contain a very large number of different ions. Note that, in common usage, the term ‘molten salt’ has also come to mean mixtures of salts, although the term itself clearly indicates a single compound.

In principle (in fact an important thermodynamic principle), the IL obtained by mixing Na[fsi] and [C_3mpyr][NTf_2] is exactly the same as that obtained by mixing the appropriate quantities of Na[NTf_2] and [C_3mpyr][fsi]. The points of origin are irrelevant in defining the IL; only the quantities of the individual ions present are important. In fact, such ILs with very high concentrations of Na or Li salts are proving to be highly effective as electrolytes for Na and Li batteries [1].

Some definitions of IL add a temperature range, such as ‘below 100 °C’, to the definition but this is not necessary. In fact, it is limiting to do so, since it can blinker our perspective on which compounds or mixtures may be useful for certain applications. Indeed, there are many, quite valuable, applications of ILs at temperatures above 100 °C, for example, the preparation of MnO_x water oxidation catalysts by electrodeposition at 130 °C [2]. The key requirement for this is that the IL be a liquid at 130 °C. It is convenient if it is also liquid at room temperature, but it is not necessary for this to be the case and one should certainly not exclude from consideration compounds having melting points >100 °C for an application such as this. Similarly, a definition that includes ‘a salt having a melting point below 100 °C’ (or some other temperature such as room temperature) is also an unnecessary restriction because in some cases the melting point may be practically difficult to find and measure. The supercooling of liquids below their equilibrium melting points is a well-known phenomenon, and in some cases the liquid becomes so viscous that the crystalline phase never forms on a practical timescale. This is particularly true of mixtures of salts, which we have agreed are perfectly good ILs, because the melting points of individual compounds is often sharply depressed in mixtures. We will discuss the melting points of ILs in Chapter 2, and multicomponent phase diagrams and behavior further in Chapter 5. With all of this in mind, referring to a melting point in our definition of an IL becomes unhelpful.

Table 1.1 Glossary of structures and nomenclature abbreviations used in this book.

Quaternary cations	**Abbreviation**	**Structure**
Alkylmethylimidazolium	$[C_n\text{mim}]^+$	
Alkyldimethylimidazolium	$[C_n\text{dmim}]^+$	
Alkylmethylpyrrolidinium	$[C_n\text{mpyr}]^+$	
Alkylmethylpiperidinium	$[C_n\text{mpip}]^+$	
Ammonium	$[N_{n,n,n,n}]^+$	
Phosphonium	$[P_{n,n,n,n}]^+$	
Ether-functionalized	$[N_{R,R,R,2O1}]^+$, etc.	
Cholinium	$[Ch]^+$	
Sulfonium	$[S_{R,R',R''}]^+$	
Guanidinium	$[Gdm]^+$	

(Continued)

Table 1.1 (Continued)

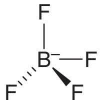
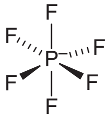
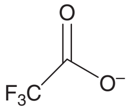
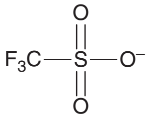
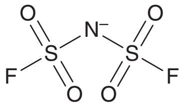
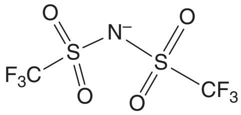
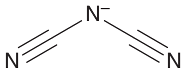
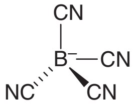
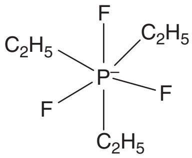
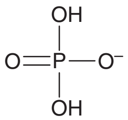
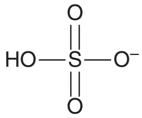
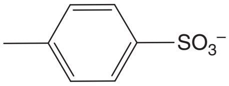
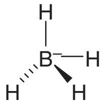
Anions	**Abbreviation**	**Structure**
Tetrafluoroborate	$[BF_4]^-$	
Hexafluorophosphate	$[PF_6]^-$	
Trifluoroacetate	$[tfa]^-$	
Triflate	$[OTf]^-$ or $[CF_3SO_3]^-$	
Bis(fluorosulfonyl)imide[a)]	$[fsi]^-$ or $[N(SO_2F)_2]^-$	
Bis(trifluoromethanesulfonyl)imide[a)]	$[NTf_2]^-$ or $[N(SO_2CF_3)_2]^-$	
Dicyanamide	$[N(CN)_2]^-$ or $[dca]^-$	
Tetracyanoborate	$[B(CN)_4]^-$	
Fluoroalkylphosphates	$[fap]^-$, $[efap]^-$, etc.	
Dihydrogenphosphate	$[H_2PO_4]^-$ or $[dhp]^-$	

Table 1.1 (Continued)

Anions	Abbreviation	Structure
Hydrogen sulfate	$[HSO_4]^-$	
p-Toluenesulfonate or tosylate	$[Tos]^-$	
Tetrahydroborate or borohydride	$[BH_4]^-$	

a) Also referred to as 'amides'.

The meaning of the word 'ion' in this definition also needs some discussion. Species such as Cl^- are obvious, as are simple molecular ions such as $[NO_3]^-$. Things become more subtle when we consider metal coordination complex ionic species such as $[AlCl_4]^-$, which were used extensively during the early work on ILs, as reviewed briefly in the following. These are certainly ionic as written, and as long as they continue to stay bound in the real liquid, for long times, then they fit our definition. However, there is always an equilibrium process by which such complex species are formed, and therefore we must always recognize the presence, in equilibrium, of some amount of the component species. In the case of $[AlCl_4]^-$, this might be Al^{3+} and Cl^-; as long as these components involved are also ionic, we still have an IL, although with more complex 'speciation' than is at first apparent. This speciation, and how it responds to variables such as temperature, can influence the IL's properties significantly.

In the case of $Co(H_2O)_6{}^{2+}$, which sits in equilibrium with H_2O and Co^{2+}, the situation is more complicated; $[Co(H_2O)_6][NO_3]_2$ is a simple hydrate salt that melts into a stable liquid at 55 °C. Where the other species are neutral (e.g., H_2O), we have non-ionic components intruding into our IL and at some stage we must begin to think of the liquid as a mixture rather than a pure IL (recall that our definition includes the word 'entirely'). It becomes important to consider where the dividing line lies between a 'pure' IL, meaning containing only the ions we think are present, and a 'mixture' of ions and other species. MacFarlane and Seddon proposed some time ago that a practical approach to this problem be adopted based on the fact that very few of any of our laboratory chemicals are absolutely pure – in fact, 100% purity is a practical impossibility. So, in reality, we may accept something as 'pure' if it is at least 95% of the desired compound – or perhaps 99% for high-quality/sensitivity work. Another perspective, which underlies much of our laboratory chemistry, is that we consider something to be pure if the level of contaminants (often starting with water and the ever-present dissolved N_2 and O_2) is not sufficient to *significantly* affect its properties; this requires thought, judgment, and discussion of what is 'significant'. This, quite reasonable, practical approach avoids pedantic arguments about whether something does or does not fit our definition of an IL. This also allows our definition to cover a host of very interesting and important complex-ion species.

Therefore, to summarize, throughout this book we will simply refer to an IL as being any 'liquid that is comprised entirely of ions', with the word 'entirely' being used in a practical rather than absolute sense. Although our definition now includes the classical field of molten salts, we will focus mostly on the ambient-temperature ILs that have become of immense interest in the last 20 years.

Other types of liquid systems that may be considered related to ILs but fall outside of our definition, and are not covered here, are liquid mixtures of ions with molecular species or ions with water. These complex liquid systems have been discussed in a number of recent reviews and books [3–7].

1.3 A Brief Perspective

In this book we will discuss many of the different types of ILs now available and the applications being developed. However, it is also important to appreciate the origins of this field and the path through different ion chemistries that has led us this point. As our definition above highlights, it is a mistake to put ILs and high-temperature molten salts into two separate classifications and treat them as different fields. While this book primarily concentrates on those species that are air- and water-stable and liquid at room temperature, because those are the focus of the majority of present research reports, other salt families also have much to teach us [8, 9].

The first 'discovery' of a room-temperature IL is often attributed to Paul Walden who made ethyl ammonium nitrate, which is a protic ionic liquid (a class of IL discussed further below) [10]. He recognized that the low melting point (13–14 °C) was a result of the larger organic cation that decreases the degree of ion association compared to an inorganic salt. It is also likely that liquid organic salts were recognized by organic chemists with annoyance long before Walden, when they probably described them as 'intractable oils' and disposed of them.

Remarkably, the ability of ammonium salts to dissolve cellulose was first recognized in 1934 [8, 11]; the use of ILs for processing biomass (which commonly includes cellulose) is now an important and extensive area of investigation, discussed in more detail in Chapter 6.

Angell and his group began to investigate ambient-temperature systems in the 1970s [12], and then in the 1980s chloroaluminate-based salts were developed that combined pyridinium or imidazolium cations with the tetrachloroaluminate anion ($[AlCl_4]^-$), again demonstrating the value of a large organic cation in reducing the melting point [9, 13, 14]. Depending on the composition, some of these salts are liquid at room temperature and primarily found application in batteries and metal electrodeposition. However, the composition of these materials is quite complex as, depending on the relative concentrations of the two components, they can also form multivalent species such as $[Al_2Cl_7]^-$ and have either (Lewis) acidic, neutral, or basic properties. These ILs (and their starting materials) are also very moisture sensitive, with $[AlCl_4]^-$ hydrolyzing to form corrosive HCl, which severely limits their application.

One of the most significant advances in the evolution of ILs came with the discovery of air- and water-stable species in 1992 [15] by Wilkes and his group. This report combined the 1-ethyl-3-methylimidazolium cation ($[C_2mim]^+$, which is still one of the most widely used cations today) with $[BF_4]^-$, $[NO_3]^-$, $[NO_2]^-$, and acetate anions. We now know that some fluorinated anions (e.g., $[BF_4]^-$ and $[PF_6]^-$) are in fact susceptible to hydrolysis [16], particularly at increased temperatures, and produce HF. Nonetheless, the significantly improved stability that these anions impart compared to the chloroaluminates is highly beneficial.

From this point in time, the field of ILs expanded rapidly, both in terms of the different ions used and in the range of applications being investigated. These applications include those on a research lab-scale and also an industrial scale; the commercial use of ILs has been under development since the late 1990s [8]. Table 1.1 shows the structures and common abbreviations of the most widely used IL ions. It can be seen that there are a variety of different fluorinated anions in use because these commonly produce low melting points, relatively low viscosities, and good electrochemical stability. This is primarily a result of the charge delocalization over the anion (because F is so electronegative). The relationship between the chemical structure of ILs and the different physical properties (viscosity, melting point, etc.) is discussed throughout this book. The $[NTf_2]^-$ anion is a classic example of a fluorinated anion [17, 18], and for the same reasons as this is attractive for IL electrolytes, it has also been widely used in the battery community for many years (originally just as the lithium salt, $Li[NTf_2]$).

The cations used to make ILs are still predominantly nitrogen-based, although phosphonium cations are becoming increasingly common and can impart better stability [19, 20]. Methods for synthesizing common nitrogen-based ILs are discussed in Chapter 4. Another emerging family of ILs comprises ‘solvate ionic liquids’, which are concentrated mixtures of salts and a solvent – most commonly lithium salts and oligoether (also known as ‘glyme’) solvents [21, 22]. The multiple oxygens on the glyme strongly solvate the lithium ion, essentially forming a $[Li(glyme)]^+$ cation that is balanced by the counter-ion from the lithium salt (most commonly $[NTf_2]^-$). Thus, they have a relatively ionic nature and similar behavior to ILs (e.g., low vapor pressure) despite the presence of a molecular component. Not all concentrated mixtures of lithium salt and solvent form ‘solvated ILs’, that is, if the coordination of the Li^+ is not strong enough. In that case, the physical properties of the mixture would not be consistent with a pure cation/anion combination and would therefore fall outside our definition of an IL. However, many concentrated mixtures do form ‘solvated ILs’ and these show great promise in various battery applications [21, 22].

While much of the early work on ILs/molten salts was driven by interest in their use as electrolytes, the potential benefit of these materials to ‘green chemistry’ – on a lab scale and in industry – has also been an important driving force. However, ILs should not be claimed as ‘green’ solvents simply because they have negligible vapor pressure (and thus do not emit the toxic vapors of many volatile organic solvents). Factors such as biodegradation, toxicity, and recycling of the IL must also be considered. The ‘12 Principles of Green Chemistry’

[23] also include parameters such as reducing the number of reaction steps, minimizing overall energy consumption, and decreasing the amount of materials used, which are as important for designing green engineering processes; all of these must be considered before classifying the use of an IL as 'green'. The toxicity and biodegradation of ILs is discussed further in Chapter 9.

Finally, one other frequently proclaimed feature of ILs is their 'tunability'. Once we understand that we can use large charge-diffuse ions to decrease the melting point of high-temperature molten salts, then we realize that there are an extraordinarily large number of ions that we can choose from to make our IL. Therefore, if we know which properties the different ions will produce, we can 'tune' the IL to suit our application (e.g., choosing a fluorinated anion to increase the electrochemical stability or decrease miscibility with water). The phrase 'task-specific' ionic liquid is sometimes used, which originally referred to the use of functionalized alkyl groups to improve the partitioning of specific metal ions into the IL phase from water [24], but this terminology has since expanded in scope. The use of IL mixtures to achieve the desired properties allows a further dimension in tunability, and this is discussed further in Chapter 5. In general, however, we are still some way from being able to design a cation/anion combination from first principles to optimize a specific physical property. The reasons for this will likely become clearer as we progress through this book and the complexity of the relationships between the chemical and the physical properties of ILs is discussed further. In the future, computational techniques for modeling ILs, which are introduced briefly in the following and in Chapter 5, are likely to bring significant benefit toward 'designing ILs to suit the task'.

1.4 Aprotic Versus Protic ILs

Thus far we have discussed ions that do not contain any labile (or transferable) protons; these are called 'aprotic' ILs meaning 'not protic'. On the other hand, ILs can actually be formed by proton transfer from a Bronsted acid to a Bronsted base, and these are termed 'protic ionic liquids' (PILs). This family has some unique characteristics that need additional consideration with respect to how they fit within our definition of an IL.

The physical properties of PILs can depend very strongly on the relative strengths of the acid and base, as this determines the extent of proton transfer to form the salt:

$$\mathrm{HA} + \mathrm{B} \rightleftharpoons [\mathrm{BH}^+][\mathrm{A}^-] \tag{1.1}$$

The free-energy change associated with the proton transfer process, as well as the relationship between this and ΔpK_a (the difference between the pK_a values of the acid and base), has a direct influence on properties of the liquid such as its vapor pressure, which in this case is nonzero at most temperatures, and its 'ionicity' (as discussed further in Chapter 5). This is because the free-energy change determines the extent of proton transfer and thus the amount of free acid and base present in the PIL. It was this problem that prompted Seddon and MacFarlane to propose the 95% (or 99%) guideline discussed above as a practical definition of when these could be called ILs. The presence of these neutral species affects the melting point (one could think of these as impurities within the PIL). Also, it can be difficult to remove all traces of water from PILs, as extended drying under vacuum will remove the volatile acid or base components, shifting the above equilibrium and changing the composition.

It is important to note that the acid/base stoichiometry in a PIL does not have to be 1 : 1; in fact, it is quite hard to achieve genuinely 1 : 1 stoichiometry. The actual composition can impact significantly the chemical and thermal properties of the liquid [25, 26]. Such off-stoichiometry compositions must also be considered to be mixtures in most cases – the melting behavior of mixtures is also discussed further in Chapter 5.

1.5 An Overview of IL Applications

When considering all the different applications of ILs, of which there is an ever-growing number, it is useful to relate these back to their unique properties. We often introduce ILs as having properties that can include 'low melting point, negligible vapor pressure, good electrochemical and thermal stability, and tunable structures', and so forth, although it is very important in such an introduction to note that not all ILs have all of these properties. So how do these characteristics translate to application, and which properties still need the most investigation and improvement? The following provides some examples of particular properties attracting certain applications.

The low melting point of ILs drives interest in their use as pharmaceutical salts, where the cation or anion is an active pharmaceutical ingredient [27–29]. The low melting point removes the concern of a salt crystallizing into an alternative polymorph (crystal structure) from that which has been trialed and patented, as the formation of polymorphs has significant medical and legal implications. Having the drug in a liquid form may also make it easier to be administered to patients. This application of ILs is discussed further in Chapter 9.

The ionic nature of ILs also means that they provide quite unique solvation environments compared to conventional molecular solvents, and this is exploited in a variety of different synthetic reactions, materials processing/extraction, and gas separation (as discussed further in Chapter 6). There is also extensive interest in their use for biomass processing. Biomass is a complex mixture of materials that can include cellulose, hemicellulose, keratin, lignin, chitin, and so on, depending on its source, and it is a valuable sustainable resource. However, these material mixtures are notoriously insoluble in molecular solvents, which makes their chemical processing difficult. ILs are being investigated for both the dissolution of a variety of different biomaterials and for their processing into higher value products [29, 30]. For biotechnological applications, the ability of ILs to dissolve and stabilize enzymes and proteins, DNA, and RNA is also extremely valuable. Note, however, that in these applications often the IL must contain a small amount of water, and therefore they are sometimes referred to as 'hydrated ILs'. These applications are discussed further in Chapter 9.

Unique solubilizing properties, coupled with good electrochemical stability, also underlie the use of ILs for rare-earth processing and recycling [31]. Rare-earth metals are used in significant quantities globally as they have unique magnetic, luminescent, and electrochemical properties, but supplies are increasingly becoming limited. ILs are promising for two techniques – as an ionic extractant for the separation of rare-earth salts, and as the medium for the subsequent electrodeposition of the pure rare-earth metal. The electrodeposition of rare-earth metals requires very electrochemically stable, aprotic media, and until recently this process has primarily utilized high-temperature molten salts. The use of ILs for the electrodeposition of a variety of metals is discussed in Chapter 7.

Excellent electrochemical stability is arguably one of the most important characteristics of some ILs, as evidenced by their extensive use in electrochemical devices, for electrowinning, water splitting, and so on [32–34]. Water splitting describes the electrolysis of water into hydrogen and oxygen. This is of great interest for the large-scale production of hydrogen as a fuel, particularly if the energy for the electrolysis can be provided by the sun (i.e., photoelectrochemical water splitting). Central to this process is an efficient electrocatalyst for the water oxidation reaction, as it is the kinetics of this reaction that is the more limiting factor. ILs have been used as a medium for the synthesis of good water-splitting catalysts such as MnO_x, where x is typically between 1.5 and 2 [2]. Although these deposition and oxidation processes are still under investigation, one of the key properties of the IL here appears to be the structure that it imparts to the liquid phase (and the liquid/electrode interphase) during the reaction, which influences the thermodynamics of the process. The use of ILs to enhance the water oxidation reaction (i.e., decrease the overpotential) is also central to their use in metal–air batteries. The use of ILs in electrochemical processes and devices is discussed in Chapters 7 and 8.

In addition to the synthesis of water-splitting catalysts mentioned previously, ILs have, of course, found application in a wide range of other synthetic reactions – organic, inorganic, biological, and so on. Again, related to the unique properties of ILs, the benefits of their use are multifold. Most simply, the ability to dissolve materials that are insoluble in common organic solvents is highly advantageous, while their ionic nature helps in stabilizing nanoparticle dispersions during synthesis. At a more sophisticated level, the term 'ionothermal synthesis' describes the use of ILs as both the solvent and as a structure-directing tool [29, 35]. This has been widely utilized for the synthesis of a range of valuable materials including molecular sieves, metal–organic frameworks (MOFs), reduced graphene oxides, and polyoxometalates, during which the nature of the IL used can impact the resultant material structure. In this application, the low vapor pressure and good thermal stability of ILs also provide an important advantage: such reactions use temperatures up to 200 °C, and therefore if water is used (i.e., in 'hydrothermal synthesis'), this requires the reaction to be performed in an autoclave. In contrast, the ionothermal reaction can often be carried out in ordinary equipment. However, while the templating effects of ILs for the synthesis of these materials are intriguing, full understanding or control of the self-assembly processes that underlie such synthesis requires further investigation. The nature of the IL and their structure (in the liquid phase and at solid/liquid interfaces) also influence the synthesis of a variety of nanoparticles [36]. The structural ordering of ILs, as well as its impact on some synthetic processes, is discussed in Chapter 3.

Other synthetic applications of ILs include the use of chiral ILs in stereoselective synthesis, where they can be used as the catalyst or as the synthetic medium [37]. Here, the most important and unique property of the IL is the ability to incorporate a chirally pure moiety into the ionic structure, the source of which may be natural (e.g., amino acid-based ILs) or synthetic. Chiral ILs also have application in chromatography and spectroscopy, for example, as NMR chiral shift reagents.

In addition to chiral catalysis, ILs can also be used for heterogeneous, homogeneous, and biocatalysis (whole-cell and enzyme-catalyzed). This is a very wide-ranging application of ILs and is the focus of multiple books and reviews [38–40], and is discussed further in Chapter 6. In this application there are two important material classes: supported ILs, that is, the use of a porous solid support to immobilize an IL containing a dissolved homogeneous metal catalyst, and 'solid catalyst with IL layer', where a heterogeneous catalyst is coated with an IL to improve the properties [40]. In terms of the application of ILs in the liquid form, these are commonly used in a biphasic system with another solvent. In this application, the solubilizing properties of the IL are the key.

Although it is not yet a large field, it is interesting to note the use of ILs as heat transfer fluids, as this is an example of an application that benefits from the relatively high heat capacity and good thermal stability of ILs. For this application, low vapor pressures, viscosity, and corrosivity are also important requirements. Nanoparticles can also be added to the IL to improve the heat capacity and thermal conductivity [41, 42].

In the field of energetic materials [43], the huge structural variability of ILs is a great advantage, as are their low vapor pressure, wide liquid range, and good thermal stability. Energetic materials are those with a large amount of stored chemical energy that can be released by, for example, shock, heating, or applying friction, and are thus used as explosives, propellants, and so on. As one class of such materials, 'hypergolic ILs' refer to ILs designed to ignite when in contact with a suitable oxidizer. These ILs are being designed as a replacement for hydrazine, which is highly toxic and difficult to handle, for use in propellants. Nitrogen-containing heterocyclic cations (e.g., substituted alkyl ammonium, imidazolium, or triazolium cations) are commonly combined with anions such as nitrate, dicyanamide, nitrocyanamide, cyanoborate, azide, or aluminum borohydride (which contain energetic groups $-NO_2$, $-N_3$, $-CN$, etc.). Although these salts are often solid at room temperature, and even above 100 °C, they still fit within our definition of ILs and are the subject of a significant number of research efforts.

The use of ILs in tribology, that is, as lubricants to reduce the wear and friction between two moving parts, benefits primarily from their low vapor pressure, good thermal stability, synthetic versatility, and the ability to interact strongly with different surfaces. This includes, in some cases, forming surface films that are composed of IL degradation products. Another possible advantage is the ability to control the viscosity, which is an important determinant of lubrication performance, by using IL mixtures. There is a very large potential commercial market for this particular IL application. Cations with long alkyl chains are frequently used, as these have structural similarity with the common base oils, typically with fluorine- and phosphorous-containing anions, for example, $[NTf_2]^-$ or diphenyl phosphate [44, 45]. ILs can also be mixed with the base oils that are currently used; the IL thus replaces the normal additives. This also reduces the cost associated with the IL, as less quantity is needed while still maintaining the efficacy of lubrication [46]. However, achieving miscibility of the IL with these relatively nonpolar materials can be a challenge.

Finally, another application for ILs with significant commercial potential is their use in sensors. Here we are primarily referring to electrochemical sensors, where the wide electrochemical window and nonvolatility of ILs are a considerable advantage. Often, for this application the IL is used to modify an electrode surface (e.g., glassy carbon, platinum, or graphite) or used as a layer on a quartz crystal microbalance. Two important uses of IL-based sensors are the detection and quantification of gases and of biological species. For both chemical and biological sensing, the ability to optimize the solubility of the target analyte by tuning the nature of the IL ions is very important [47, 48].

1.6 Key Properties and Techniques for Understanding ILs

The above discussion gives an indication of how different applications benefit from the properties of ILs. To further develop such applications, it is important to fully understand the origin and unique characteristics of ILs. This understanding will then allow us to design anions and cations that impart further improvements in IL properties and performance. In this section we introduce the key properties of ILs that we are commonly most interested in and the techniques that are available for probing them.

1.6.1 Viscosity

One of the holy grails of IL research is achieving lower viscosities, as this would enable further improvements in the performance of electrochemical devices through improved ion transport, make lab-scale use easier, simplify the design of fluid handling for commercial processors, and so on. The viscosity of ILs is relatively high compared to other solvents – at least 10 times higher than water and often significantly greater (think of the consistency of oil or even honey). This is a result of the strong intermolecular interactions: van der Waals forces, hydrogen bonding, and Coulombic forces. The viscosity of neat ILs and their mixtures is discussed further in Chapter 5. Mixing ILs with molecular solvents is a very effective way of reducing the viscosity, but this generally comes at the expense of an increase in vapor pressure, flammability, lower electrochemical stability, and so on. As with many of the other properties of ILs, experimental measurement of the viscosity requires a clean and dry

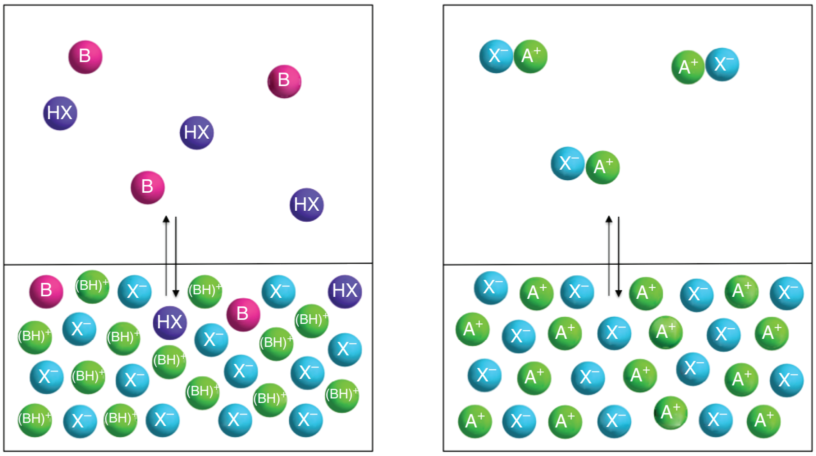
IL and measurement under an inert atmosphere. This should be taken into consideration when selecting the viscometer to be used, as should be the sample size required (which, for ILs, we normally want to be as small as possible) and the Newtonian or non-Newtonian behavior of ILs.[49]. If the IL behaves as a Newtonian fluid, that is, the viscosity does not change with sheer rate, then the viscosity can be accurately measured by rolling-ball, capillary, or rotational (e.g., cone and plate) viscometers. To assess the non-Newtonian viscosity of an IL (or of an IL containing an additional dissolved or suspended species as this often introduces non-Newtonian behavior), a rotational viscometer is to be used. Further, magnetic resonance velocity imaging is a recently reported technique that allows magnetic resonance images to be collected within the cone and plate viscometer [50]. This allows further information about the rheological behavior of ILs with and without suspended nanoparticles to be obtained. The rheological behavior of ILs may also be related back to the effect of ordering of the liquid structure of ILs [51, 52], which is discussed further in Chapters 3 and 5. Finally, it is useful to note that the viscosity of ILs decreases relatively rapidly with temperature, and this effect can be utilized for ease of handling in the lab or in larger scale commercial reactor design.

1.6.2 Vapor Pressure

Negligible vapor pressure is arguably the physical property of ILs most commonly referred to as beneficial for application but one of the least investigated. For example, how does this depend on the nature of the IL and what exactly do we mean by ‘negligible’? (Note that we should never say ‘no vapor pressure,’ as this is a thermodynamic impossibility, except at absolute zero kelvin). Contrary to the initial understanding in the field, Earle and coworkers famously showed that some aprotic ILs are, in fact, distillable and therefore must have a significant vapor pressure [53]. One technique for quantifying this as a function of temperature is a combination of the Knudsen effusion apparatus and a quartz crystal microbalance [54, 55]. Note that our discussion of vapor pressure of aprotic ILs is fundamentally of different origin from the vaporization of PILs, which occurs by evaporation of the constituent acid and base (see Eq. 1.1) as neutral molecules into the gas phase. Aprotic ILs are now believed to exist in the gas phase as strongly associated ion pairs (Figure 1.1), which is supported by both experimental and computational studies [56, 57]. Information about the enthalpy of vaporization of ILs also helps us to understand the strength of interactions between ions in the liquid phase. More comprehensive studies of the vapor pressure of different ILs and an understanding of the gas-phase structures are seen as important areas of future study.

1.6.3 Melting Point

The other often-reported property of ILs is the low melting point, the origin of which is discussed in Chapter 2. However, we still have to learn much before we can quantitatively understand how different ions affect this property and how we can therefore design new low-melting species. The most common technique for measuring the melting point is differential scanning calorimetry (DSC).



Protic ionic liquid

Aprotic ionic liquid

Figure 1.1 Illustration of the difference between the volatilization of PILs, where neutral species evaporate into the gas phase and aprotic ILs that exist as tightly bound ion pairs in the gas phase. (Adapted from Earle *et al.* 2006 [53]. Reproduced with permission of Nature Publishing Group.)

Measurement of melting point can also be complicated by the tendency of many ILs to supercool and form glasses, which is another property that is significantly affected by impurities in the IL.

1.6.4 Nanostructure

A more complex characteristic of ILs is the formation of nanometer-level structure in the liquid phase. This is not commonly described as an advantage but is certainly quite special and can have a significant influence on the properties and behavior of ILs (and reactions in ILs). As discussed in detail in Chapter 3, this is still a young area of study, in which techniques such as X-ray and neutron diffraction are predominantly used to reveal the nanometer-level detail [58]. The structure of ILs at surfaces, including at solid surfaces such as inorganic nanoparticles in the IL, and at interfaces (liquid/liquid or liquid/gas) is even more complex but equally important, as it impacts the behavior of ILs in many applications.

1.6.5 Thermal Properties

There is a range of thermal properties that are important for IL applications. Most important and most widely referenced is their thermal stability; unfortunately, this is often overestimated. Commonly, thermal gravimetric analysis (TGA) is used, where the IL is heated at a controlled rate and the decrease in mass of the sample analyzed. The onset of decomposition is then taken from the intersection of the initial baseline with the tangent of the plot over the region of most rapid weight loss. However, weight loss of the IL will have occurred before this 'onset' point; it has simply not been allowed sufficient time to become significant at the heating rate used, because the experiment is normally relatively fast (e.g., 10 °C min^{-1}). More useful data is the maximum recommended operating temperature of that IL below which degradation is negligible, quantification of the *rate* of decomposition, and an understanding of the decomposition products [59]. This latter information can be obtained by a TGA coupled to a mass spectrometer or by using pyrolysis mass spectrometry. This is discussed in Chapter 5.

The thermal conductivity of ILs is of great importance to their application as, for example, heat transfer fluids. However, there has been little experimental measurement or theoretical prediction of this property [60]. The most common experimental approaches to this measurement involve either placing the IL between two parallel plates, one of which is then heated, or inserting a heating wire into the sample. The thermal conductivity is then calculated from either the heat flow from the upper plate through the IL to the cooling plate, or the heating rate of the wire. The appropriate mathematical relationship must then be used to take into account the setup geometry used and separate out the thermal conductivity and thermal diffusivity of the IL.

The heat capacity of ILs (the quantity of heat required to raise the temperature by 1°C) is also crucial for their application as heat transfer fluids and is another property not widely studied [61, 62], or predicted [63]. DSC and modulated DSC are the most common methods of measurement, although other types of calorimetry can also be used. The heat capacity generally increases linearly with the molar mass of the IL, but for mixtures of ILs this becomes more complex. The heat capacity and thermal conductivity of ILs are discussed further in Chapter 5.

In many applications, such as the use of ILs in batteries or synthesis, it is very important to know about the potential for 'thermal runaway' during heating, which can cause explosions. If the heat produced in a reaction or, for example, at an electrode surface is greater than the capacity for the IL to remove that heat, then the system will self-heat and thermal runaway can occur. The likelihood of this happening for different ILs can be measured by accelerating rate calorimetry (ARC). This is a seldom-used technique but one that provides crucial information regarding the safe use of ILs. In this method, the IL is heated in small temperature steps, and at each step the instrument detects whether an exothermic process is occurring, that is, heat is being released, as opposed to the IL being able to stabilize at that temperature. In one study [64], for a series of $[\text{C}_2\text{mim}]^+$ ILs, no self-heating was observed with the $[\text{BF}_4]^-$, $[\text{NTf}_2]^-$, or diethylphosphate anions, which is the behavior desired for their use as solvents or electrolytes. However, ILs with the $[\text{fsi}]^-$, $[\text{B(CN)}_4]^-$, and tricyanomethanide anions exhibited exothermic self-heating behavior and an accompanying pressure increase, with onset temperatures of 165, 316, and 230 °C, respectively. What this means, in a practical sense, is that, if these ILs are exposed to temperatures in excess of these 'onset temperatures,' then extreme temperature and pressure rises could spontaneously occur and, for example, sealed battery packs may burst open. This ARC technique can also be used to assess the thermal runaway characteristics of IL electrolytes containing lithium salts and common Li-ion battery electrode materials and compare the behavior to that of the commercially used carbonate electrolytes. This has confirmed [C_2mim][fsi] to be the worst IL among those tested, and indicates that not all ILs are better (in this regard) than the carbonate solvents [65].

1.6.6 Electrochemical Properties

Finally, it is primarily the electrochemical properties of ILs that enable their extensive use in batteries, supercapacitors, fuel cells, solar cells, electrowinning, and so on. By 'electrochemical properties' we are predominantly referring to good electrochemical stability and relatively high ionic conductivity. The specific behavior of ILs in batteries, their interfacial stability, and the formation of a passivating 'solid electrolyte interface' are discussed in Chapter 8. Characterization of the electrochemical stability of ILs is usually performed using cyclic voltammetry, as discussed in detail in Chapter 7. Here, in terms of the thermodynamics of the process, it is the structure of the cation and the anion that defines the oxidative and reductive stability of the IL: the most positive or negative potential that the IL can be exposed to without an electron-transfer reaction occurring, resulting in reduction of the cation or oxidation of the anion. However, the kinetics of these reactions and, thus, the behavior of the IL in actual applications depend on factors such as the nature and morphology of the electrode surface, the strength of interactions at the IL/surface, the structure of this surface layer (and how far these layers penetrate into the bulk IL), temperature, IL viscosity, and conductivity.

The arrangement of an IL at an electrode surface is defined by the 'electric double layer', which describes how the potential decreases with the distance from the electrode surface. It is this phenomenon that forms the basis of double-layer capacitor operation, but understanding the potential profile across ILs is also very important for other electrochemical devices. Analyzing the structure of ILs at electrode surfaces (and how this changes with the potential of the surface) is extremely complex. Ideally, such analysis would be performed *in situ* (i.e., allowing us to look at the structure of an IL within an actual battery, fuel cell, etc.), but using *ex situ* experiments such as atomic force microscopy (AFM) to gain a picture of the arrangements of ILs on different solid surfaces (charged or uncharged) can also be extremely informative [58, 66].

1.6.7 Conductivity and Ion Transport

The performance of ILs in an electrochemical device is influenced not only by the structure but also, very importantly, by the dynamics of the ions. Achieving a high rate of transport of the electroactive species to and from the electrode surface is crucial, and this is where ionic conductivity, diffusion rate of the electroactive species, and the transport number become relevant. The ionic conductivity, measured by electrochemical impedance spectroscopy (EIS), tells us about the average transport of all charged species – the IL, plus any other dissolved electroactive ions such as lithium salts. To obtain more species-specific transport information, cyclic voltammetry (CV)-based techniques can be used to measure the diffusion rate of just the electroactive species through the solution [67].

This parameter is primarily affected by the viscosity of the IL. CV analysis is also used to assess the metal deposition/stripping behavior of ILs containing, for example, dissolved Li or Na salts. Measurement of the transport number (the fraction of charge carried by, for example, the Li^+ ion in an IL/Li salt battery electrolyte solution) can be calculated from the steady-state current produced after holding a potential across the electrolyte for an extended period [68].

It is also interesting to note that the conductivity of ILs can tell us about the extent of ion pairing or aggregation in the liquid. It is a result of this ion aggregation that the conductivity of ILs is often not nearly as high as we might expect if we were to simply consider the high concentration of ions – if these ions were all free to move independently, the ionic conductivity would be much greater than we actually observe. We can also compare the conductivity obtained from standard electrochemical measurements (which measure the migration rate of species in an applied electric field and thus is applicable only to charged species) with that predicted from NMR diffusion measurements (which measure the diffusion of all species, charged or not). If we use the Nernst–Einstein equation to predict the conductivity based on the diffusion data from NMR experiments, then the difference between this value and the actual conductivity (which is always lower) tells us about the extent of ion aggregation in the IL [69]. This ion aggregation parameter is commonly referred to as the 'ionicity' and is discussed in detail in Chapter 5.

1.6.8 Computational Techniques

There are many theoretical approaches that can help us to understand the chemical and physical properties of ILs. This field has benefited enormously from improvements in program sophistication and computer power (which is necessary for the study of large systems) since the first computational studies of ILs [70]. The techniques used for understanding and predicting the physical properties of ILs can generally be grouped into five categories [71], with roughly increasing levels of complexity:

- those that correlate the physical properties of an IL with molecular volume or density,
- those that correlate the molecular structure of ILs using 'molecular descriptors' (electronic, geometric, etc.), with their properties, (e.g., the quantitative structure–property relationship QSPR approach),
- molecular dynamics (MD) simulations [72], which allow, as the name suggests, investigation of the molecular/ionic structure and interactions in an IL and also their dynamics (i.e., transport),
- *ab initio* theory [73], where quantum chemistry principles are used to study the energetics and structure of the ions and clusters of ions *from first principles* using electronic wave functions, and
- a combination of the third and fourth techniques, termed *ab initio* MD [74].

We will discuss the application of computational techniques to investigation of the physical properties of ILs throughout the book, for example, for melting point in Chapter 2, liquid-phase structure in Chapter 3, and transport properties in Chapter 5.

One of the key difficulties of this field is that no single technique is accurate for the simulation of all short- and long-range interactions, for the incorporation of all enthalpy and entropy factors, for accurate simulation of the force fields (the energy functions used to describe the potential energy of the system), and for looking at the dynamics of the IL. Thus there is always a trade-off between high accuracy and the scale of simulation that is feasible, i.e., how many ions can be studied within a given amount of expensive computer time and over how long a time period. It is therefore up to the researcher to select the most appropriate technique for their research while being aware of the associated limitations of the technique. What is also important is to relate the results of theoretical predictions back to the results of any experimental measurements available.

1.7 New Materials Based on ILs

As the field has progressed, a variety of IL-related materials have been developed, where the IL is a starting point but has been designed to exhibit solid-like mechanical properties for applications where this is desirable. In the following, we look briefly at some of these important material classes and give suggestions for further reading on these subjects.

IL-based polymer electrolytes are arguably one of the most commercially viable applications of ILs (at least in the near future). This is driven by a rapidly expanding battery market, for example, for large-scale stationary storage, electric vehicles, support for domestic photovoltaics and portable electronics, and improving the safety of these devices. Here we are predominantly referring to IL-based electrolytes incorporating Li^+ salts, although next-generation batteries based on other ions, such as Na^+, are under development. ILs can potentially be used to replace the flammable and volatile organic solvents currently used in commercial Li ion batteries, and also avoid the use of $Li[PF_6]$ that decomposes to produce highly toxic HF. The use of ILs, in their liquid form, in electrochemical devices is discussed in Chapter 8. The benefit of using an IL within a polymeric or otherwise solidified system is that it prevents leakage, for example, if the battery is damaged, and provides a mechanical barrier to the growth of lithium dendrites that can cause short-circuiting and fire. The most common class are those formed by IL addition, effectively as a plasticizer, to a polymer/Li salt system such as $PEO/Li[NTf_2]$ [75]. When the IL becomes a major component, these materials are also commonly referred to as gels or ionogels. However, the extensive field of solid or gel IL-based electrolytes also encompasses polymerized ILs, zwitterionic gels (where the cation and anion are covalently tethered), those solidified using inorganic nanoparticles, and ILs with alkoxy-silane functional groups attached to the cation. Central to the development of all of these material classes for use in lithium batteries is achieving sufficient transport of the target Li^+ ion. Low transport rates is one of the primary limitations of present solid-state IL-based battery electrolyte materials and the focus of an extensive research effort [76, 77].

The development and use of IL-based gels is not restricted to the battery field – other types of IL gels have application in electrochemical devices (fuel cells, electrochromics, supercapacitors, etc.), in catalysis, and in separation and analysis, for example, as the stationary phase for gas chromatography [78]. The combination of ILs and polymers is also widely used in applications such as CO_2 separation [79], polyelectrolyte membrane fuel cells [80, 81], and actuators [33]. The concept of 'IL-based gels' encompasses a wide range of materials, including two-phase heterogeneous mixtures of IL with polymers, ceramics, carbon-based materials, metal nanoparticles, or macromolecules. Central to all of this research is the desire to maintain or even improve the desirable properties of the IL, such as the wide electrochemical window, low volatility, and ion conduction, while also achieving the advantages of a solid-state material such as mechanical strength, reduced leakage, increased device stability, or even the incorporation of additional functionality such as catalysis [82].

Polymerized ILs, or poly(ionic liquids), are another approach to combining the advantageous properties of ILs and polymers [83, 84]. Analogous to many of the applications of IL-based gels, these can be used as electrolytes in batteries, fuel cells, supercapacitors, and so on, as gas separation membranes, and also as solid supports for catalytic materials [78]. The synthesis of these materials is discussed in Chapter 4.

A further class of solid-like IL-based material is obtained by impregnating the IL within porous solid supports such as silica, activated carbons, porous glasses, or MOFs [85, 86]. This encompasses materials known as 'supported ionic liquid phase' (SILP) catalysts [87], which are based on thin films of ILs on high-surface-area solid supports: these are used to immobilize transition-metal catalysts. The properties of the IL-impregnated material depend on the amount of IL on the surface: that is, whether it is present as a monolayer that may be covalently bound to the surface, or as a multilayer. Multilayer systems allow the dissolution of additional species, such as catalysts, acids, or nanoparticles. The primary applications of ILs coated on solid supports are catalysis, for example, using transition metals, enzymes, acids, or nanoparticles within the IL, and separation technologies such as gas purification and CO_2 separation. ILs on a surface, or confined into a small space [88], can behave quite differently from the bulk IL. Therefore, understanding the properties and structure of ILs on surfaces is crucial for developing their application [58, 89].

ILs on solid supports, such as silica columns, can also be used as stationary phases for chromatographic applications [90–92]. Gas and liquid chromatography both benefit from the low vapor pressure and thermal stability of ILs, while the nature of the cation and anion can be used to adjust the retention behavior of the column and even allow separation of both polar and nonpolar analytes. Capillary electrophoresis, where the IL is again supported on a column, and mass spectroscopy techniques such as matrix-assisted laser desorption/ionization MALDI, where the IL provides the matrix, are other analytical applications.

Finally, in our discussion of porous supports, it is interesting to note that ILs are also good precursors for the synthesis of carbon-based materials. Heating the IL (protic or aprotic, or polymerized ILs) at high temperatures results in carbonization. This can produce carbon-based materials with well-controlled morphology and heteroatom doping, such as the incorporation of N atoms within the carbon structure. The heteroatoms are very important for achieving the desired catalytic properties for the carbon structures. ILs with cross-linkable groups, such as nitriles, are particularly good for this application, as cross-linking occurs during heating and helps in producing well-controlled morphologies and a more even distribution of the N dopants [32, 93, 94].

1.8 Nomenclature and Abbreviations

The full names of many ILs are very long and unwieldy, so a range of more simplified names and acronyms are commonly used. Table 1.1 summarizes the common names, structures, and recommended abbreviations that are used in this book. Following recommended inorganic nomenclature, acronyms such as $[dca]^-$ are in lower case letters in square brackets. Charges are shown on isolated ions but not when part of an ion pair. Atomic ions are shown without brackets.

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