Abstract

Ionic liquids (ILs), considered to be a relatively recent magical chemical due to their unique properties, have a large variety of applications in all areas of the chemical industries. The areas of application include electrolyte in batteries, lubricants, plasticizers, solvents and catalysis in synthesis, matrices for mass spectroscopy, solvents to manufacture nano-materials, extraction, gas absorption agents, etc. Non-volatility and non-flammability are their common characteristics giving them an advantageous edge in various applications. This common advantage, when considered with the possibility of tuning the chemical and physical properties of ILs by changing anion–cation combination is a great opportunity to obtain task-specific ILs for a multitude of specific applications. There are numerous studies in the related literature concerning the unique properties, preparation methods, and different applications of ILs in the literature. In this review, a general description of ILs and historical background are given; basic properties of ILs such as solvent properties, polarity, toxicology, air and moisture stability are discussed; structure of ILs, cation, anion types and synthesis methods in the related literature are briefly summarized. However, the main focus of this paper is how ILs may be used in the chemicals processing industries. Thus, the main application areas are searched and the basic applications such as solvent replacement, purification of gases, homogenous and heterogeneous catalysis, biological reactions media and removal of metal ions are discussed in detail. Not only the advantages of ILs but also the essential challenges and potentials for using ILs in the chemical industries are also addressed. ILs have become the partner of scCO\textsubscript{2} in many applications and most of the reported studies in the literature focus on the interaction of these two green solvents, i.e. ILs and scCO\textsubscript{2}. The chemistry of the ILs has been reviewed in numerous papers earlier. Therefore, the major purpose of this review paper is to provide an overview for the specific chemical and physical properties of ILs and to investigate IL–scCO\textsubscript{2} systems in some detail. Recovery of solutes from ILs with CO\textsubscript{2}, separation of ILs from organic solvents by CO\textsubscript{2}, high-pressure phase behavior of IL–scCO\textsubscript{2} systems, solubility of ILs in CO\textsubscript{2} phase, and the interaction of the IL–scCO\textsubscript{2} system at molecular level are also included.

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Keywords: Ionic liquids; Supercritical carbon dioxide; Review
1. General description of ILs

Ionic liquids (ILs) have been accepted as a new green chemical revolution which excited both the academia and the chemical industries. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new syntheses. The terms room temperature ionic liquid (RTIL), nonaqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase [1]. ILs are known as salts that are liquid at room temperature in contrast to high-temperature molten salts. They have a unique array of physico-chemical properties which make them suitable in numerous applications in which conventional organic solvents are not sufficiently effective or not applicable. Short [2] pointed out in 1980, that there were only a few patent applications for ILs, in 2000, the number of patent applications increased to 100, and finally by 2004, there were more than 800. This is a clear indication of the high affinity of the academia and industry to the ILs.

2. History of ILs

ILs have been known for a long time, but their extensive use as solvents in chemical processes for synthesis and catalysis has recently become significant. Welton [1] reported that ILs are not new, and some of the ILs such as [EtNH3][NO3] was first described in 1914 [3]. The earliest IL in the literature was created intentionally in 1970s for nuclear warheads batteries [4]. During 1940s, aluminum chloride-based molten salts were utilized for electroplating at temperatures of hundreds of degrees Celsius. In the early 1970s, Wilkes tried to develop better batteries for nuclear warheads and space probes which required molten salts to operate [4]. These molten salts were hot enough to damage the nearby materials. Therefore, the chemists searched for salts which remain liquid at lower temperatures and eventually they identified one which is liquid at room temperature. Wilkes and his colleagues continued to improve their ILs for use as battery electrolytes and then a small community of researchers began to make ILs and test their properties [5,6]. In the late 1990s, ILs became one of the most promising chemicals as solvents.

The first ILs, such as organo-aluminate ILs, have limited range of applications because they were unstable to air and water. Furthermore, these ILs were not inert towards various organic compounds [7]. After the first reports on the synthesis and applications of air stable ILs such as 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]) and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]), the number of air and water stable ILs has started to increase rapidly [7]. Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications such as replacing them with volatile organic solvents, making new materials, conducting heat effectively, supporting enzyme-catalyzed reactions, hosting a variety of catalysts, purification of gases, homogeneous and heterogeneous catalysis, biological reactions media and removal of metal ions [4].

Some of the basic physical properties of ILs such as density and viscosity are still being evaluated by the researchers since the study of the IL is a relatively young field [8]. The number of research on ILs and their specific applications is increasing rapidly in the literature. For example, the cation 1-n-ethyl-3-methylimidazolium has been the most widely studied until 2001, and nowadays, 1-3-dialkyl imidazolium salts are the most popularly used and investigated class of ILs. For the future of ILs, the aim of research is the commercialization of ILs in order to use them as solvents, reagents, catalysts and materials in large-scale chemical applications.

3. Basic properties of ILs

ILs are made of positively and negatively charged ions, whereas water and organic solvents, such as toluene and dichloromethane, are made of molecules. The structure of ILs is similar to the table salt such as sodium chloride which contains crystals made of positive sodium ions and negative chlorine ions, not molecules. While, salts do not melt below 800 °C, most of ILs remain liquid at room temperature. The melting points of sodium
chloride and lithium chloride are known as 801 and 614°C, respectively. Since these conventional molten salts exhibit high melting points, their use as solvents in applications is severely limited. However, RTILs are liquid generally up to 200°C. ILs have a wide liquidus range. The adopted upper melting temperature limit for the classification as ‘IL’ is known as 100°C and higher melting ion systems are generally referred to as molten salts.

Researchers explained that ILs remain liquid at room temperature due to the reason that their ions do not pack well [9]. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point [10]. Most widely used ILs and their structures are given in Table 1.

As solvents, ILs possess several advantages over conventional organic solvents, which make them environmentally compatible [1,4,8,10–15]:

- ILs have the ability to dissolve many different organic, inorganic and organometallic materials.
- ILs are highly polar.
- ILs consist of loosely coordinating bulky ions.
- ILs do not evaporate since they have very low vapor pressures.
- ILs are thermally stable, approximately up to 300°C.
- Most of ILs have a liquid window of up to 200°C which enables wide kinetic control.
- ILs have high thermal conductivity and a large electrochemical window.
- ILs are immiscible with many organic solvents.
- ILs are nonaqueous polar alternatives for phase transfer processes.
- The solvent properties of ILs can be tuned for a specific application by varying the anion cation combinations.

Generally, the above statements are valid for the most commonly used ILs. However, one should note that there are many ILs containing different anions and cations and their properties cover a vast range. Therefore, the above statements should not be generalized for all existing ILs and for those designed in the future.

ILs exhibit the ability to dissolve a wide variety of materials including salts, fats, proteins, amino acids, surfactants, sugars and polysaccharides. ILs have very powerful solvent properties such that they can dissolve a wide range of organic molecules, including crude oil, inks, plastics, and even DNA [9].

Two important groups of ILs are those based on imidazolium and pyridinium cations with PF_{6}− and BF_{4}− anions [13,14]. Figs. 1 and 2 illustrate the imidazolium and pyridinium derivatives of ILs and their possible anions which are extensively investigated in literature.

ILs tend not to give off vapors in contrast to traditional organic solvents such as benzene, acetone, and toluene. The vapor pressures of the ILs are extremely low and are considered as negligible. For example, Kabo et al. [16] gave the vapor pressure of [bmmim][PF_{6}] at 298.15 K as 10^{−11} Pa. ILs are introduced as green solvents because unlike the volatile organic compounds (VOCs) they replace, many of these compounds have negligible vapor pressure, they are not explosive and it may be feasible to recycle and repeatedly reuse them. It is more convenient to work with ILs in the laboratory since the non-evaporating properties of ILs eliminate the hazardous exposure and air pollution problems.

ILs 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 and positively charged large cations, and these specific ILs may be utilized to dissolve a certain 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. The physical and chemical properties of ILs are varied by changing the alkyl chain length on the cation and the anion. For example, Huddleston et al. [17] concluded that density of ILs increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion.

Although ILs are studied by a great number of research groups, there are still many questions that scientist are not able to answer. For example, one of the basic rules of chemistry “like dissolves like” is seem to be broken by some ILs: Nonpolar benzene is up to 50% soluble (by volume) in polar tetrachloroaluminate-based ILs [9]. Therefore, studies on why ILs are able to dissolve uncharged covalent molecules are continuing.

Until recently, ILs have been considered to be scarce but it is now known that many salts form liquids at or close to room temperature. There are literally billions of different structures that may form an IL. The composition and the specific properties of these liquids depend on the type of cation and anion in the IL structure. By combining various kinds of cation and anion structures, it is estimated that 10^{18} ILs can be designed [18,19].
<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Structure</th>
<th>Short name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butyl-3-methylimidazolium tetrafluoroborate</td>
<td><img src="image1" alt="Structure" /></td>
<td>[bmim][BF4]</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium triflate</td>
<td><img src="image2" alt="Structure" /></td>
<td>[bmim][TfO]</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium methide</td>
<td><img src="image3" alt="Structure" /></td>
<td>[bmim][methide]</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium dicyanamide</td>
<td><img src="image4" alt="Structure" /></td>
<td>[bmim][DCA]</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate</td>
<td><img src="image5" alt="Structure" /></td>
<td>[bmim][PF6]</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium nitrate</td>
<td><img src="image6" alt="Structure" /></td>
<td>[bmim][NO3]</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide</td>
<td><img src="image7" alt="Structure" /></td>
<td>[bmim][Tf2N]</td>
</tr>
<tr>
<td>1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide; R = C₆H₁₇</td>
<td><img src="image8" alt="Structure" /></td>
<td>[hmim][Tf2N]</td>
</tr>
<tr>
<td>1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide; R = C₈H₁₇</td>
<td><img src="image9" alt="Structure" /></td>
<td>[omim][Tf2N]</td>
</tr>
<tr>
<td>2,3-Dimethyl-1-hexylimidazolium bis(trifluoromethylsulfonyl) imide</td>
<td><img src="image10" alt="Structure" /></td>
<td>[hmim][Tf2N]</td>
</tr>
</tbody>
</table>

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3.1. Solvent properties of ILs

Both the chemical industry and academia search for alternative solvents to meet the cleaner technology requirements since the most widely used solvents are volatile and damaging. ILs are good solvents for a wide range of substances; organic, inorganic, organometallic compounds, bio-molecules and metal ions. They are usually composed of poorly coordinat-
ing ions which makes them highly polar but non-coordinating solvents. ILs are immiscible with most of the organic solvents, thus they provide a nonaqueous, polar alternative for two-phase systems [19]. Furthermore, 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 potential as solvents, ILs can easily replace other conventional organic solvents which are used in large quantities in chemicals processing industries to eliminate major environmental problems.

Many chemical reactions are carried out in conventional solvents. Upon the completion of reaction, chemical products must be taken out of the solvent. There are several techniques to recover a product from a solvent: For example, water-soluble compounds may be extracted with water; distillation may be used for chemicals with high vapor pressures. On the other hand, for the chemicals with low vapor pressures, distillation must be performed at low pressures, which may not be economical. In addition to this, there are some chemicals that can decompose as a result of heating, such as pharmaceuticals. Therefore, ILs seem to be potentially good solvents for many chemical reactions in the cases where distillation is not practical, or water insoluble or thermally sensitive products are the components of a chemical reaction. Although, ILs are not considered to be distilled due to their low volatility, Earle et al. [20] showed that many ionic liquids, especially bistriﬂamide ILs, can be distilled at 200–300°C and low pressure without decomposition. It was once more understood that there is a long way for total investigation of the properties of ILs. The authors suggested that the possibility of IL distillation introduced a new method for IL purification, and also new application areas (such as isolation of highly soluble products by high-temperature crystallization) could emerge. But, distillation still cannot be applied when heat-labile products are encountered in ILs.

In most chemical applications, extraction is used for separation since it is an energy efﬁcient technique. Generally, extraction consists of two immiscible phases such as an organic phase and an aqueous phase. Many organic solvents used in extractions are known with their ﬂammable and toxic properties. In order to improve the safety and environmental friendliness of this conventional technique, ILs may be used as ideal substitutes due to their stability, nonvolatility and adjustable miscibility and polarity [15].

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 [1,21]. Charge distribution on the anions, H-bonding ability, polarity, dispersive interactions are the main factors that inﬂuence the physical properties of ILs [22]. For example, imidazolium-based ILs are highly ordered hydrogen-bonded solvents and they have strong effects on chemical reactions and processes.

### 3.2. Polarity of ILs

Polarity of chemicals is commonly used to classify the solvents. The terms used as polar, nonpolar and apolar are generally related to the values of dielectric constants, dipole moments, polarizabilities. If a solvent has the ability to dissolve and stabilize dipolar or charged solutes, it is defined as a polar solvent. Under this simple deﬁnition, ILs are highly polar solvents, but it is not completely true to make such strict conclusions since there ILs can be designed in a vast range.

The existences of polar and nonpolar domains, believed to be associated with the unique “amphiphilic” solvent properties of ILs, are found in the structures of PF6− and BF4− salts [23]. Since polarity is the simplest indicator of solvent strength, researchers compared polarities of ILs and conventional solvents: Carmichael and Seddon [24] showed that 1-alkyl-3-methylimidazolium ILs with anions [PF6], [BF4], [(CF3SO2)2N], and [NO3] are in the same polarity region as 2-aminoethanol and lower than alcohols such as methanol, ethanol and butanol, Aki et al. [25] indicated that [bmmim][PF6], [C8mim][PF6], [bmmim][NO3] and [N-bupy][BF4] are more polar than acetonitrile and less polar than methanol and these ILs are expected to be at least partially miscible with water. ILs based on [PF6] anion is preferred as solvents in most extraction application to form biphasic systems due to their immiscibility with water.

### 3.3. Toxicology of ILs

The green character of ILs has been usually related with their negligible vapor pressure; however their toxicology data have been very limited until now. Several authors [26–29] already mentioned this lack of toxicological data in the literature [30]. Although ILs will not evaporate and thus will not cause air pollution, it does not mean that they will not harm the environment if they enter. Most of ILs are water soluble and they may enter the aquatic environment by accidental spills or effluents. The most commonly used ILs [bmmim][PF6] and [bmmim][BF4] are known to decompose in the presence of water and as a result hydroﬂuoric and phosphoric acids are formed [31]. Therefore, both toxicity and ecotoxicity information which provide metabolism and degradability of ILs are also required to label them as green solvents or investigate their environmental impact.

The ecotoxicological studies performed to understand the effects of different ILs on enzymatic activities, cells and microorganisms are utilized to obtain LC50 levels (lethal concentration). Decreasing LC50 values indicate higher toxicities according to the toxicity classes of Hodge and Sterner scale (1956) [32]. This scale indicates that the LC50 value (in terms of mg/L) of 10 or less shows that the chemical is extremely toxic, LC50 value between 10 and 100 shows that chemical is highly toxic, LC50 value between 100 and 1000 shows that chemical is slightly toxic, and finally LC50 value between 1000 and 10,000 means that chemical is practically nontoxic.

The impact of ILs on aquatic ecosystems is highly important since some of ILs have a high solubility in water. Maginn [33] provided the LC50 levels for two imidazolium-based ILs with
chemistry in all research papers due to their nonvolatile nature. Therefore, different authors attached significant importance to proper analysis to the purity of the IL studied. Therefore, different authors account during the toxicological study of the ILs is to pay attention to the purity of the IL studied. Therefore, different authors attached significant importance to proper analyzing techniques [30]. ILs are introduced under the concept of green chemistry in all research papers due to their nonvolatile nature.

The environmental persistence [34,40] of commonly used ILs, along with their possible toxicity should be taken into account. There are still very few results about the (eco)toxicological effect of ILs and they can be evaluated more satisfactorily as green solvents or not after more data on the subject will be provided. The possible toxic and non-biodegradable nature of the existing ILs also led to the development of new types of nontoxic and biodegradable ILs [40–46].

### 3.4. Air and moisture stability of ILs

The stability of ILs is crucial for optimum performance. Many of ILs are both air and moisture stable, some are even hydrophobic. On the other hand, most imidazolium and ammonium salts are hydrophilic and if they are used in open vessels, hydration will certainly occur. The hydrophobicity of an IL increases with increasing length of the alkyl chain [25]. Despite their wide spread usage, ILs containing PF$_6^−$ and BF$_4^−$ anions have been reported to decompose in the presence of water, giving off HF. Wasserscheid et al. [47] pointed out that ILs containing halogen anions generally show poor stability in water, and also give off 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 degree to which this hydration is a problem depends on the application. For instance, small amounts of highly reactive species which are used as catalysts may be deactivated by even very small amounts of water. For this kind of application, ILs must be handled under an inert atmosphere. Moreover, the solutes used may be sensitive for air or moisture, thus an inert atmosphere is required for the IL–solute systems.

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$_6^−$ [48]. However, $Tf_2^−N^−$ 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 infra-red (IR) studies of Cammarata et al. [31] demonstrated that the water molecules absorbed from the air are mostly present in the free state, bonded via H-bonding with the PF$_6^−$ and BF$_4^−$ anions. The presence of water may have dramatic effect on IL reactivity. Since water is present in all ILs, they are usually utilized after a moderate drying process.

The new ILs synthesized are more stable than the old halogenoaluminate systems. Certain ILs incorporating 1-dialkyl imidazolium cations are generally more resistant than traditional solvents under harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes [10].

### 4. Structure and synthesis of ILs

There are a great number of different cation and anion combinations to synthesize IL. Different types of ILs give an opportunity to modify the physical and chemical properties of the IL. The most widely used cations are imidazolium, pyridinium, phosphonium and ammonium. The properties of ILs

<table>
<thead>
<tr>
<th>Compound</th>
<th>LC$_{50}$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim][PF$_6^−$]</td>
<td>250–300</td>
</tr>
<tr>
<td>[bmim][BF$_4^−$]</td>
<td>225–275</td>
</tr>
<tr>
<td>Acetone</td>
<td>30.642</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>310</td>
</tr>
<tr>
<td>Toluene</td>
<td>60–313</td>
</tr>
<tr>
<td>Benzene</td>
<td>203</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5–86</td>
</tr>
<tr>
<td>Phenol</td>
<td>5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.53–4.94</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.028</td>
</tr>
</tbody>
</table>

*Daphnia magna*, common fresh water crustaceans. Due to the reason that *D. magna* are filter feeders at the base of the aquatic food chain, their responses to ILs are essential to understand how these new solvents may impact an environmental ecosystem. As ILs, 1-n-butyl 3-methylimidazolium cation with PF$_6^−$ and BF$_4^−$ anions are used and the results are tabulated in Table 2: These two ILs are as toxic to *Daphnia* as benzene and even far more toxic than acetone, but much less toxic than ammonia, chlorine, phenol, etc. Wells and Coombe [34] also provided the results of freshwater ecotoxicity tests of some common ILs with imidazolium, ammonium, phosphonium and pyridinium cations on invertebrate *D. magna* and the green alga *Pseudokirchneriella subcapitata* (formerly known as *Selenastrumcapricornutum*). The results were reported using medium effective concentration (EC$_{50}$) values. The toxicity values of the most toxic IL were four orders of magnitude more than the least toxic IL. There was a relation between the order of toxicity and alkyl side chain length of the cation. For alkyl methylimidazolium ILs with C$_4$ side chain constituents showed moderate toxicity, whereas the C$_{12}$, C$_{16}$, and C$_{18}$ species were very highly toxic to both organisms under investigation. Pyridinium, phosphonium, and ammonium species with C$_4$ side chain constituents had also only moderate toxicity, whereas C$_6$ and longer side chains showed significant increases in toxicity. It was shown that the least toxic ionic liquids’ ecotoxicity were comparable to hydrocarbons’ such as toluene and xylene. The most toxic ionic liquids are many orders of magnitude more acutely ecotoxic than organic solvents such as methanol, tert-butyl methyl ether, acetonitrile, and dichloromethane. The authors also emphasized that simple acute ecotoxicity measurements did not enough to fully characterize the full impact of a solvent released to the environment but were only part of the environmental impact assessment.

There were also some studies on investigation of toxicity of ILs performed on animals such as the nematode model organism (*Caenorhabditis elegans*) [35], freshwater pulmonate snails (*Physa acuta*) [36], Fischer 344 rats [37] and zebra fish (*Danio rerio*) [38].

One of the most important points that must be taken into account during the toxicological study of the ILs is to pay attention to the purity of the IL studied. Therefore, different authors [35,39] attached significant importance to proper analyzing techniques [30]. ILs are introduced under the concept of green chemistry in all research papers due to their nonvolatile nature.
Fluorinated anions tend to be expensive and in response to cost and safety concerns new ILs with non-fluorous ions have been introduced. In the synthesis of these ILs, anions are derived from inexpensive bulk chemicals. Alkylsulfate anions are the most popular non-fluorous anions due to their nontoxic and biodegradable structures. The first commercially available IL for which toxicology data are available contains alkylsulfate anion (methosulfate) [50].

4.2. Cations

The cation of IL is generally a bulk organic structure with low symmetry. Most ILs are based on ammonium, sulfonium, phosphonium, imidazolium, pyridinium, picolinium, pyrroldinium, thiazolium, oxazolium and pyrazolium cations. The research mainly focuses on RTILs composed of asymmetric $N,N$-dialkylimidazolium cations associated with a variety of anions. $1-n$-butyl-3-methylimidazolium and $1-n$-ethyl-3-methylimidazolium are the most investigated structures of this class.

Chiappe and Pieraccini [18] indicated that the melting points of the most ILs are uncertain since ILs undergo considerable supercooling. Therefore, 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. The melting point of ILs is essential because it represents the lower limit of the liquidity and with thermal stability it defines the interval of temperatures within which it is possible to use ILs as solvents [18].

4.3. Synthesis

There are three basic methods to synthesize ILs: metathesis reactions, acid–base neutralization, direct combination [1]. Many alkylammonium halides are commercially available; they can also be prepared 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 [1]. Tetraalkylammonium sulfonates are also prepared by mixing sulfonic acid and tetraalkylammonium hydroxide [51]. 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. Halogenaoluminate and chlorocuprate ILs are prepared by this method. The synthesis methods of ILs have been given in numerous articles [52–56].

5. Major applications suggested for ILs

The research areas on ILs are growing very rapidly and the potential application areas of ILs are numerous. The unique
chemical and physical properties of ILs bring about several application areas including reaction and synthesis media. The application areas of ILs can be expressed as solvents for organic, organometallic synthesis and catalysis; electrolytes in electrochemistry, in fuel and solar cells; lubricants; stationary phases for chromatography; matrices for mass spectrometry; supports for the immobilization of enzymes; in separation technologies; as liquid crystals; templates for synthesis nano-materials and materials for tissue preservation; in preparation of polymer–gel catalytic membranes; in generation of high conductivity materials; catalytic membranes; in generation of high conductivity materials; for liquid–liquid equilibria data for the ternary systems are reported. Moreover, binary temperature–composition curves of ILs with alcohols, alkanes, aromatics and water; ternary temperature–composition curves of ILs with alcohols and water; solubilities of some organics and water in ILs are all investigated by various groups to completely benefit from the solvent properties of ILs [62–64].

Arce et al. [65] studied essential oil terpenless by extraction using organic solvents or ILs. Citrus essential oil is simulated as a mixture of limonene and linalool and 2-butene-1,4-diol and ethylene glycol are used as solvents. They choose 1-ethyl-3-methylimidazolium methanesulfonate as the IL and liquid–liquid equilibria data for the ternary systems are reported. Arce et al. [65] concluded that IL presents the highest selectivity but close to the other organic solvents and they reported that the results for solute distribution ratio depend on the concentration range of extraction.

5.2. Purification of gases

Reliable information on the solubility of gases in ILs is needed for the design and operation of any possible processes involving IL. Processes using ILs to purify gas streams were developed after solubilities of various gases in ILs were reported by some researchers [66–68]. These experimental studies show that some gases, especially CO2 is highly soluble in ILs. The simulations performed explain that the anion of the IL is responsible for high gas solubility. With this property ILs, can be replaced as solvents in reactions involving gaseous species.

Anthony et al. [69] investigated solubility of nine different gases up to 13 bar: carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen, and nitrogen in [bmim][PF6]. These gases were chosen for several reasons: CO2 solubility is important due to the possibility of using scCO2 to extract solutes from ILs; ethylene, hydrogen, carbon monoxide, and oxygen are reactants in several types of reactions studied in IL such as hydroformylations, hydrogenations, and oxidations. Due to the nonvolatile nature of IL, the gas solubilities in IL were measured using a gravimetric technique, usually with a microbalance. The study of Anthony et al. [69] showed that CO2 has the highest solubility and strongest interactions with [bmim][PF6], followed by ethylene and ethane. Argon and oxygen had very low solubilities and immeasurably weak interactions. Fig. 5 demonstrates the solubility of various gases (CO2, CH4, C2H6, CH4, Ar, O2) in [bmim][PF6] at 25 °C and at different pressures. Except for CO2, all gases remained in the Henry’s law regime up to 13 bar. However, CO2 showed some non-linearity, indicating some degree of saturation. Henry’s constants of these gases in various organic solvents and in [bmim][PF6] were compared and the results showed that the gases that are less soluble in the IL are less soluble in the other solvents as well. However, CO2 is more soluble in the IL than in the other solvents. The relatively high solubility of CO2 was explained as a result of its large quadrupole moment. The solubility of CO2 in [bmim][PF6] at different temperatures is demonstrated in Fig. 6.
Camper et al. [66] measured the solubility of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} in [bmim][PF\textsubscript{6}], [emim][Tf\textsubscript{2}N], [emim][CF\textsubscript{3}SO\textsubscript{3}] (ethylmethylimidazolium trifluoromethanesulfone), [emim][dca] (ethylmethylimidazolium dicyanamide) and [thtdp][Cl] (tributylhexadecylphosphonium chloride) to demonstrate that the regular solution theory can be used to model the gas solubilities in RTILs at low pressures and studied the effects on pressure and the temperature on the solubility of gases in RTILs. The previous works; Blanchard et al.[70] and Anthony et al. [71] related that the solubility of the gases in ILs to the intermolecular interactions between the anion of the IL and the gas. On the other hand, Camper et al.[66] indicated that at low pressures, the solubility of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} may be explained using the regular solution theory without considering the intermolecular interactions between the anion of the IL and the gas. At higher pressures, regular solution theory is limited and Camper et al. [66] attributed this limitation to the dominant entropic effects.

Recently, the results of solubility of hydrogen in [bmim][PF\textsubscript{6}] was presented for temperatures from 313 to 373 K and pressures up to 9 MPa. The results demonstrated that the solubility of hydrogen in [bmim][PF\textsubscript{6}] is low and increases slightly with temperature [72]. Since ILs can dissolve certain gaseous species, they may be used in conventional gas absorption applications. The nonvolatility of ILs prevent any cross contamination of the gas stream by the solvent during the process. Moreover, regeneration of the solvent may be performed easily by a simple flash or distillation to remove the gas from the solvent without any cross contamination. The other advantages of ILs as separating agents are no solvent loss and no air pollution. Currently, researchers are interested in examining the potential of ILs for the separation of CO\textsubscript{2} from flue gases emitted from fossil–fuel combustion operations [73]. ILs may also be utilized as supported liquid membranes. In conventional membranes, gas dissolves in liquid but then the liquid in which the gas dissolved evaporates rendering the membrane useless [50]. Due to the nonvolatility of ILs, they can be immobilized on a support and used in supported liquid membranes.

ILs are also used for storage and delivery of hazardous specialty gases such as phosphine (PH\textsubscript{3}), arsine (AsH\textsubscript{3}) and stibine (SbH\textsubscript{3}). GASGUARD® Sub-Atmospheric Systems supply the major ion implant gases: AsH\textsubscript{3}, boron trifluoride (BF\textsubscript{3}), enrich boron trifluoride (\textsuperscript{11}BF\textsubscript{3}) and PH\textsubscript{3} sub-atmospherically [74]. The system is combined with gas supply technologies for the delivery of the gases when needed. In the complexed gas technology, the desired gases (BF\textsubscript{3} and PH\textsubscript{3}) are chemically bond to ILs sub-atmospherically, then pulling the vacuum on the IL–gas complex provides the mechanism to evolve high purity gas, similar to desorbing a gas from active carbon.

5.3. Homogenous and heterogeneous catalysis

One of the most important targets of modern chemistry is to combine the advantages of both homogenous and heterogeneous catalysis [75]. Greater selectivity is generally observed in homogenous catalysis compared to its heterogeneous counterparts, but separation of the catalyst from the product stream or from the extract stream causes a problem [8]. ILs offer the advantages of both homogenous and heterogeneous catalysts with their two main characteristics: A selected IL may be immiscible with the reactants and products, but on the other hand the IL may also dissolve the catalysts. ILs combine the advantages of a solid for immobilizing the catalyst, and the advantages of a liquid for allowing the catalyst to move freely [76]. Brennecke and Maginn [8] indicated that the ionic nature of the IL also gives an opportunity to control reaction chemistry, either by participating in the reaction or stabilizing the highly polar or ionic transition states.

ILs have an active role in chemical reactions and catalysis. Some of the examples where ILs are utilized are: reactions of aromatic rings; clean polymerization [77]; Friedel Crafts alkylation [78]; reduction of aromatic rings [79]; carboxylation [80]; halogenation [81]; oxidation [82]; nitration [83]; sulfonation [84]; solvents for transition metal catalysis; immobilization of charged cationic transition metal catalysis in IL phase without need for special ligands [85]; in situ catalysis directly in IL rather than aqueous catalysis followed by extraction of products from solution: this process eliminates washing steps, minimizes losses of catalysis and enhances purity of the products [86].
Many applications of ILs in catalytic reactions can be found in various articles in the literature [1,12,85,87–89].

Holbrey and Seddon [90] described many of the catalytic processes which use low temperature ILs as reaction media and indicated that the classical transition metal catalyzed hydrogenation, hydroformylation, isomerization, dimerization and coupling reactions can be performed in IL solvents. In their review, Holbrey and Seddon [90] concluded that ILs may be used as effective solvents and catalysts for clean chemical reactions instead of the volatile organic solvents.

Brennecke and Maginn [8], concluded that ILs have been used successfully for hydrogenations, hydroformylations, isomerizations, dimerizations, alkylations, Diels-Alder reactions and Heck and Suzuki coupling reactions, and in general researchers have concluded that the reaction rates and selectivities are as good or better in ILs than in conventional organic solvents. The catalytic hydrogenation of cyclohexene using rhodium-based homogenous catalysts [91] and hydrogenation of olefins using ruthenium and cobalt-based homogenous catalyst [92] in various ILs are studied and the results indicated that there is a certain increase in the reaction rates and selectivity compared to the other normal liquid solvents.

Lagrost et al. [12] used imidazolium and ammonium-based ILs ([emim][NTf2], [bmim][NTf2], [bmim][PF6], [(C8H17)3NCH3][NTf2]) as reaction media for different types of electrochemical reactions and investigated the oxidation of organic molecules (anthracene, naphthalene, durene, 1,4-dithiafulvene and veratrole) in ILs. Their results suggest that the nature of investigated mechanisms is almost unchanged in ILs as compared with the conventional organic media although the structure of molecular solvents and ILs are expected to be quite different. Lagrost et al. [12] also concluded that the diffusion coefficient of the organic compounds are about 100 times smaller than those in conventional media as expected from the lower viscosity of RTILs versus organic solvents. The positive results of this study demonstrated that ILs can be used as a new media for organic electrochemistry [12].

5.4. Biological reactions media

ILs are used in biological reactions such as the synthesis of pharmaceuticals due to the stability of enzymes in ILs, and in separation processes such as the extraction of amino acids [15]. IL biphasic systems are used to separate many biologically important molecules such as carbohydrates, organic acids including lactic acid [93,94]. Carbohydrates are renewable and inexpensive sources of energy and raw material for the chemical industry. The underivatized carbohydrates are not soluble in most of the conventional solvents although they are soluble in water. Their insolubility in most solvents prevents the transformation of carbohydrates. Therefore, the ability of ILs to dissolve carbohydrates enables transformation possibilities [15,93,95,96].

Lau et al. [95] studied the alcoholysis, ammoniolysis, and perhydrolysis reactions by *Candida antarctica* lipase catalysis using the [bmim][PF6] and [bmim][BF4] as reaction media. Reaction rates were generally comparable with, or better than, those observed in organic media. Park and Kazlauskas et al. [96] studied the acetylation of 1-phenylethanol catalyzed by lipase from *Pseudomonas cepacia* (PCL) in several ILs and the reaction was as fast and as enantioselective in ILs as in toluene. They also investigated the acetylation of glucose catalyzed by lipase B from *C. antarctica* (CALB) and found that the transformation was more regioselective in ionic liquids because glucose is up to one hundred times more soluble in ionic liquids. Liu et al. [93] stated that carbohydrates are only sparingly soluble in common organic solvents as well as in weakly coordinating ionic liquids, such as [bmim][BF4]. They found that ILs that contain the dicyanamide anion could dissolve approx. 200 g L⁻¹ of glucose, sucrose, lactose and cyclodextrin and the esterification of sucrose with dodecanoic acid in [bmim][dca] could be performed with CALB.

Swatloski et al. [97] showed that ILs can also be used as non-derivatizing solvents for cellulose, the most abundant biorenewable material. Cellulose, which is insoluble in water and in most of the common organic solvents, has many derivitized products in many applications of the fiber, paper, and polymer industries. ILs incorporating anions which are strong hydrogen bond acceptors are most effective solvents for cellulose, whereas ILs containing non-coordinating anions including PF6⁻ and BF4⁻ are not effective. Furthermore, Przybysz et al. [98] examined the influence of ILs on a cellulose product, paper and found that the wettability of paper is improved, whereas the strength decreased as a result of a weakening of cellulose hydrogen bonds.

Finally, Pfundner et al. [99] tested the water immiscible ILs namely; [bmim][PF6], [bmim][Tf2N] and [oma][Tf2N] (methyltrioctylammonium bistrifluoromethanesulfonylimide) for their biocompatibility towards *Escherichia coli* and *Saccharomyces cerevisiae*. The results of this study showed that these water immiscible ILs do not damage microbial cells and therefore one can utilize these water immiscible ILs as substrate reservoirs and in situ product extracting agents for biphasic whole cell biocatalytic processes. Generally, toxic organic solvents have been used as substrate reservoirs and with this study it is shown that water immiscible ILs may be used as biocompatible solvents for microbial biotransformations. The experimental results demonstrated that there is an increase of chemical yield from <50% to 80–90% in simple batch processes and (R)-1-(4-chlorophenyl) ethanol was produced at a higher initial reaction rate in the biphasic system (>50 μM s⁻¹ L⁻¹) compared to the aqueous system [99]. Although ILs are known by their highly viscous characteristics, good mass transfer rates were obtained in their study.

5.5. Removing of metal ions

Dai et al. [100] studied the effects of ILs (with PF6⁻ and Tf2N⁻ anions) on improving the ability of crown ethers to remove metal ions from aqueous solutions. Strontium nitrate, a fission product for which there is no available extraction technique for its removal from radioactive waste sites, was used in this study.
Visser et al. [57] designed and synthesized several ILs to remove cadmium and mercury from contaminated water. The hydrophobic ILs come into contact with contaminated water and they snatch the metal ions out of water. Task-specific ionic liquids (TSIL) concept is introduced in order to synthesize ILs with desired properties to extract metal ions. Visser et al. [57] produced TSILs by appending different functional groups (namely thiother, urea and thiourea) to imidazolium cations. These IL cations can be considered as a new IL class or a novel class of IL extractants. Synthesized TSIL cations were combined with PF$_6^-$ anion and used alone or in a mixture with [bmim][PF$_6$]. The results of the study gave significant distribution ratios for mercury and cadmium in liquid–liquid separations and stripping of metal ions from ILs into an aqueous phase such as radiochemical stability of ILs [106].

In the literature, various studies were performed to extract metal ions using ILs [108–113]. Different metal ions including alkali, alkaline earth metals, heavy metals and radioactive metals are researched by using different ILs. Generally, the side chain of the IL on the cation is varied and the effect of structure of the IL on the extraction efficiency of the metal ions is investigated. The side chain of the cation influences the hydrophobic character of the IL and thus the partition coefficient of the metal ions is affected.

Visser et al. [108] extracted Na$^+$, Cs$^+$ using [C$_n$mim][PF$_6$] ($n=4$, 6, 8); Chun et al. [109] investigated extraction of other alkali metals such as Li$^+$, K$^+$, Rb$^+$ using [C$_n$mim][PF$_6$] ($n=4$–9); Luo et al. [112,113] studied the extraction of Na$^+$, K$^+$, Cs$^+$ ions using [C$_n$mim][Tf$_2$N] ($n=2$, 4, 6, 8). Not only the alkali metals but also extraction of alkaline earth metals were studied by various groups: Visser et al. [108] removed Sr$^{2+}$ using [C$_n$mim][PF$_6$] ($n=4$, 6, 8); Bartsch et al. [110] studied the removal of Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$; Luo et al. [112,113] utilized [C$_n$mim][Tf$_2$N] ($n=2$, 4, 6, 8) to extract Sr$^{2+}$. The extraction of heavy and radioactive metals such as Cu$^{2+}$, Ag$^{+}$, Pb$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$ were studied by using [C$_n$mim][PF$_6$] ($n=4$–9) and TSILs [110,111,114].

6. Challenges of ILs

The unique properties of ILs and the ability to design their properties by choice of anion, cation and substituents create many more processing options, alternative to the ones with conventional solvents. However, high cost, lack of physical property and toxicity data restrict the advantageous use of ILs as process chemicals and processing aids at the present.

The challenges in the use of ILs must be also addressed as well as their advantages. The major challenge is the cost. A kilogram of IL costed about 30,000-fold greater than a common organic solvent such as acetone. Renner [9] reported that this cost could be reduced to approximately 1000-fold greater depending on the composition of IL and the scale of production. Wagner and Uerdingen [115] anticipated that the price of cation systems based on imidazole will be in the range of $\in$ 50–100 kg$^{-1}$ if larger quantities of ILs are produced. The price can be lowered even below $\in$ 25 kg$^{-1}$ if ILs are prepared with cheaper cation sources on a ton scale. Another estimation was done by Wasserscheid and Haumann [116]. They expected that for ‘bulk ionic liquids’ choosing proper (relatively cheap) cations and anions lead to prices approximately $\in$ 301–1 for production rates of multi-ton. Moreover, scientists emphasized that the price of the ILs may look still discouraging however, the essential factor is the price to performance ratio. If the performance of an IL is extremely higher than that of the material (solvent) it aims to replace, less amounts of the IL may be needed for a given specific job [2], thus totally or partially overcoming the price disadvantage.

The second problem is associated with the manufacturing method of ILs. In manufacturing ILs environmental issues also need to be tackled since some VOCs are used to manufacture ILs. Recently, some advanced methods have been developed in the solventless syntheses of ILs. For example, 1-alkyl-3-methylimidazolium halides have been synthesized in open containers in a microwave oven without any VOCs by Varma and Namboodiri at the Environmental Protection Agency of U.S., 2001 [9].
Researchers need to find alternative ways to recycle ILs due to the reason that many processes for cleaning up ILs involve washing with water or VOCs which creates another waste stream. This problem has been solved by adopting supercritical extraction technologies to recover the dissolved organic compounds from ILs or using membrane separation processes. However, there are other solid matrices which adsorb some part of the ILs. Thus, a second rinse would be required and this would create an aqueous waste stream that contains ILs. Despite this disadvantage there may be some cleaning applications where ILs would be attractive [8].

Incomplete physico-chemical data are another challenge for the application of ILs. At the present most available data are focused on bulk physical properties such as viscosity, density and phase transitions. Relatively little is known about the microscopic physical properties of ILs. After these properties are investigated properly and the influence of ILs on chemical reaction rates is found, new ILs with precisely tailored properties can be synthesized.

It is extremely important to obtain reliable thermophysical data and transport properties of ILs in order to make them available for many applications and to design IL-based processes efficiently. Harris et al. [117] measured the viscosities of two members of one of the most commonly studied IL groups, that are based on imidazolium cations; [omim][PF$_6$] and [omim][BF$_4$] between 0 and 80°C and at pressures to 176 MPa ([omim][PF$_6$]) and 224 MPa ([omim][BF$_4$]) with a falling body viscometer and densities between 0 and 90°C at atmospheric pressure. The bulk physical properties of most widely used ILs at wider temperature and pressure ranges are essential.

Another barrier to the large-scale application of ILs arises from their high viscosities. The viscosities of ILs are higher than most organic solvents and water, usually similar to viscosity of oils. This high viscosity may be responsible to produce a reaction in the rate of many organic reactions and even a reduction in the diffusion rates of species. Also, handling of ILs with high viscosities is difficult however; increasing temperature, changing anion–cation combinations may yield ILs with lower viscosities. To overcome mass transfer limitations in gas–IL systems resulting from high viscosity reactions using ILs may be run at high pressures and in efficient gas–liquid contacting equipment.

In chemical processing, pharmaceuticals, fine chemicals, petroleum refining, metal refining, polymer processing, pulp and paper, and textiles where a nonvolatile liquid with a wide liquidus range could work better, ILs are the best choice however, the challenges of turning ILs into useful and environmentally benign fluids must be overcome.

7. ILs and scCO$_2$ systems

Green chemistry, also known as sustainable chemistry, describes the search for reducing or even eliminating the use of substances in the production of chemical products and reactions which are hazardous to human health and environment. The goal of green chemistry is to create a cleaner and more sustainable chemistry and it has received more and more attention in recent years. Green chemistry searches for alternative, environmentally friendly reaction media as compared to the traditional organic solvents and at the same time aims at increased reaction rates, lower reaction temperatures as well higher selectivities.

The ideal situation for a safe and green chemical process is using no solvent, however most of the chemical processes depend on solvents. Some of these solvents are soluble in water and therefore they must be stripped from water before it leaves the process not only for ecological but also for economic reasons. Solvents must be recovered for recycle and reuse for an economically viable process. Water, perfluorinated hydrocarbons and supercritical fluids (SCFs) are alternative solvents which may be used in green chemistry. Among these, the most promising elements of green chemistry are ILs and scCO$_2$. The low volatility of ILs is the key property that makes them green solvents. However, this advantage also causes a problem for product separation and recovery [15]. Several techniques for solute recovery from ILs exist: volatile products can be extracted from IL by distillation or simply by evaporation. However, nonvolatile or thermo-sensitive products cannot be separated from ILs with these methods. ILs exhibiting immiscibility with water can be extracted with water to separate water-soluble solutes from IL into the aqueous phase; but this method is not suitable for hydrophilic ILs [17]. Of course, organic solvents such as hexane and toluene may be effective to recover the products from IL but this approach obviously compromises the ultimate goal of ‘green’ technologies [15]. Furthermore, the cross contamination between the phases presents another problem. Finally, another green solvent is discovered which solves all the problems and recovers various kind of solutes from ILs without cross contamination: supercritical fluids (SCFs).

SCFs are compounds which are above their critical temperature and pressure and they can be manipulated from gas to liquid like densities due to their unusual properties near the critical point. They are commercially viable solvents in several applications such as dry cleaning and polymer impregnation. scCO$_2$ is the most widely used SCF as a result of nontoxic and non-flammable characteristics. scCO$_2$ has low critical temperature and pressure and it is not expensive.

The advantages of using SCFs as extraction medium include low cost, nontoxic nature, recoverability and ease of separation from the products. SCFs have been adapted for product recovery from ILs and supercritical fluid extraction (SCE) is shown to be a viable technique with the additional benefits of environmental sustainability and pure product recovery [118]. Among the SCFs, an inexpensive and readily available one, scCO$_2$ has become a partner of IL and two environmentally benign solvents are utilized together in several applications. The volatile and nonpolar scCO$_2$ forms different two-phase systems with nonvolatile and polar ILs. The product recovery process with these systems is based on the principle that scCO$_2$ is soluble in ILs, but ILs are not soluble in scCO$_2$ [70]. Since most of the organic compounds are soluble in scCO$_2$, with the high solubility of scCO$_2$ in ILs, these products are transferred from the IL to the supercritical phase.
**Table 3**

IL–gas systems phase behaviors

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Findings</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim][PF6]–CO2</td>
<td>40, 50, and 60 °C</td>
<td>Up to 93 bar</td>
<td>As pressure increases, solubility of CO2 in the IL increases</td>
<td>[70]</td>
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<tr>
<td>[C8-mim][PF6]–CO2</td>
<td></td>
<td></td>
<td>Solubility of CO2 in IL-rich phase decreases with temperature</td>
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<tr>
<td>[bmim][NO3]–CO2</td>
<td></td>
<td></td>
<td>CO2 solubility depends on the nature of the anion and cation</td>
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<tr>
<td>[emim][EtSO4]–CO2</td>
<td></td>
<td></td>
<td>The solubility of CO2 in IL-rich phase is highest for ILs with fluorinated anions</td>
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<tr>
<td>[N-bupy][BF4]–CO2</td>
<td></td>
<td></td>
<td>The general trend of the phase behavior is almost identical for all ILs</td>
<td></td>
</tr>
<tr>
<td>[bmim][PF6]–C2H4</td>
<td>10, 25, and 50 °C</td>
<td>Up to 13 bar</td>
<td>Water and carbon dioxide exhibited the strongest interactions and the highest solubilities in [bmim][PF6], followed by ethylene, ethane, and methane</td>
<td>[69]</td>
</tr>
<tr>
<td>[bmim][PF6]–C2H6</td>
<td></td>
<td></td>
<td>Argon and oxygen both had very low solubilities and essentially no interactions with the IL</td>
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<tr>
<td>[bmim][PF6]–CH4</td>
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<td>[bmim][PF6]–Ar</td>
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<td>[bmim][PF6]–O2</td>
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<td>[bmim][PF6]–CO</td>
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<td>[bmim][PF6]–N2</td>
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<td>[bmim][PF6]–H2</td>
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<tr>
<td>[bmim][BF4]–CO2</td>
<td>20, 40, 60, 80, 100, and 120 °C</td>
<td>Up to 9.7 MPa</td>
<td>Total pressure increases linearly with increasing amount of CO2 in IL</td>
<td>[119]</td>
</tr>
<tr>
<td>[bmim][BF4]–O2</td>
<td>30–70 °C</td>
<td>Atmospheric pressure</td>
<td>CO2 is found to be one order of magnitude more soluble in the IL than O2</td>
<td>[131]</td>
</tr>
<tr>
<td>[bmim][PF6]–CO2</td>
<td>25, 40, and 60 °C</td>
<td>Up to 150 bar</td>
<td>Solubility of CO2 in ten different IL is reported</td>
<td>[121]</td>
</tr>
<tr>
<td>[bmim][PF6]–Ar</td>
<td></td>
<td></td>
<td>The solubility of CO2 is strongly dependent on the choice of the anion</td>
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<tr>
<td>[bmim][PF6]–O2</td>
<td></td>
<td></td>
<td>Increasing the alkyl chain length, increases the solubility of CO2 in IL</td>
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<tr>
<td>[bmim][PF6]–CO</td>
<td></td>
<td></td>
<td>All of the ILs expand a relatively small amount when CO2 is added</td>
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<tr>
<td>[bmim][PF6]–N2</td>
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<tr>
<td>[bmim][PF6]–H2</td>
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<tr>
<td>[emim][PF6]–CHF3</td>
<td>36.15–94.35 °C</td>
<td>1.6–51.6 MPa</td>
<td>The solubility of supercritical CHF3 in [emim][PF6] is very high. At low CHF3 concentrations (mole fraction &lt;0.5), the equilibrium pressure increases almost linearly with CHF3 concentration, whereas further increase in CHF3 concentration causes a sharp increase in the equilibrium pressure. The Peng-Robinson EoS is capable of describing the experimental bubble point data of the system satisfactorily and qualitatively predicting the solubility of the ionic liquid in supercritical CHF3. The high-pressure phase behavior of [emim][PF6]–CHF3 system was completely different from that of [bmim][PF6]–CO2. CHF3 is more soluble in the IL than CO2 at higher pressures and the IL is also more soluble in supercritical CHF3 than in supercritical CO2.</td>
<td>[142]</td>
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<tr>
<td>[emim][PF6]–CO2</td>
<td>35–93 °C</td>
<td>1.49–97.10 MPa</td>
<td>CO2 is more soluble in [bmim][PF6] than in [emim][PF6]. The general phase behavior of [emim][PF6]–CO2 and [bmim][PF6]–CO2 systems are found to be completely similar. CO2 is more soluble in [bmim][PF6] than in [emim][PF6]. The phase behaviors of the systems [emim][PF6]–CO2 and [emim][PF6]–CHF3 are different. CHF3 is more soluble in the IL than CO2 at higher pressures and the IL is also more soluble in supercritical CHF3 than in supercritical CO2.</td>
<td>[129]</td>
</tr>
<tr>
<td>[hmim][PF6]–CO2</td>
<td>25.16–90.43 °C</td>
<td>0.64–94.60 MPa</td>
<td>CO2 is more soluble in [hmim][PF6] than in [emim][PF6]. The general phase behaviors of [emim][PF6]–CO2 and [hmim][PF6]–CO2 are similar. The solubility of the IL in scCO2 phase is very low and cannot be detected.</td>
<td>[130]</td>
</tr>
<tr>
<td>[hmmim][PF6]–CO2</td>
<td>25 °C</td>
<td>Up to 1 MPa</td>
<td>A group contribution form of a non-random lattice fluid model is applied to predict the solubility of CO2 in ILs</td>
<td>[123]</td>
</tr>
</tbody>
</table>
7.1. High-pressure phase behavior of IL–CO₂ systems

Preliminary works have shown that scCO₂ extraction is a viable method for solute recovery from an IL. However, the knowledge of phase behavior of IL–CO₂ systems is an essential aspect of this methodology. scCO₂ dissolution in the IL phase is not only necessary for contact with the solute but it also reduces the viscosity of the IL and therefore enhancing the mass transfer process.

Early studies of IL–CO₂ phase behavior indicated that these systems are very unusual biphasic systems. No measurable amount of [bmim][PF₆] was soluble in the CO₂-rich phase, although a large amount of CO₂ dissolved in the IL-rich phase, reducing the viscosity of IL [70]. Blanchard and Brennecke [118] concluded that the system remained as two distinct phases even under pressures up to 400 bar. Therefore, high-pressure phase behavior of [bmim][PF₆]–CO₂ is totally different from that of any ordinary organic liquid–CO₂ systems. This different phase behavior is the key phenomena which makes extraction of solutes from IL with CO₂ attractive.

Table 3 summarizes the phase behavior studies performed for IL–gas systems, demonstrates the type of IL and gases used in these studies, the experimental conditions, the basic findings and the related references.

7.1.1. The [bmim][PF₆]–CO₂ system

The phase behaviors of IL–scCO₂ systems are studied very extensively in the literature for a better understanding of the processes involving both IL and scCO₂. Since [bmim][PF₆] is the most widely studied IL in the literature, many researchers studied the high-pressure phase behavior of the [bmim][PF₆]–CO₂ system [13,69,70,119–122].

Blanchard et al. [70] measured the high-pressure vapor–liquid phase behavior of [bmim][PF₆]–CO₂ system by using two different apparatus sets: a static high-pressure phase equilibrium apparatus and a dynamic flow apparatus. In the static high-pressure vapor–liquid equilibrium apparatus, a glass cell was loaded with a known amount of IL sample and known amounts of CO₂ were metered into the cell while the sample within was vigorously stirred to ensure equilibrium. With the assumption of pure CO₂ vapor phase, the composition of the IL-rich phase was calculated by knowing the amount of CO₂ added to the cell. At the end of the equilibration period, CO₂ was completely removed from IL phase upon depressurization. The same group also used a dynamic apparatus, i.e. a high-pressure extractor to determine the solubility of the IL in the CO₂ phase. The detailed description of these apparatus sets and experimental procedures can be found in the literature [70].

Different experimental set-ups were used by other researchers: A schematic diagram of a general IL–scCO₂ experimental apparatus, which was used to measure the solubility of CO₂ in IL ([bmim][PF₆]) is given by Kim et al. [123]. Shiflett and Yokozeki [124] measured the gas solubility and diffusivity of CO₂ in [bmim][PF₆] using a gravimetric microbalance for which the details of the experimental set-up is given in the related reference.

The solubility of CO₂ in [bmim][PF₆] was determined at 40, 50 and 60 °C and pressures up to 93 bar [70]. As the pressure increases, the solubility of CO₂ in the IL-rich phase increases but the solubility value reaches a mole fraction of 0.72 at 40 °C and 93 bar. A general rule suggests that an increase in temperature results with a decrease in the solubility of gases in liquids. As expected, the solubility of CO₂ in [bmim][PF₆] rich phase decreases with temperature. However, they noticed that the temperature dependence of the solubility is quite small in this temperature and pressure range. Another crucial point is the effect of large degree of CO₂ solubility on the viscosity of IL. The viscosity of IL decreases when a certain amount of CO₂ is dissolved in IL and this effect can easily be observed by the reduced drag on the stirring magnet when a static high-pressure vapor–liquid equilibrium set-up is used. This reduction in viscosity of the liquid facilitates the solution process.
Kamps et al. [119] presented the solubility of CO₂ in [bmim][PF₆] for temperatures 293–393 K in 20 K intervals and pressures up to about 9.7 MPa. The total pressure is plotted versus the stoichiometric molality of the gas (number of moles per kilogram of the IL) in Fig. 7. The total pressure increases linearly with increasing amount of the gas in IL. The solubility data represented by Kamps et al. [119] differ from the previously reported solubility data of Blanchard et al. [70]. The comparison of experimental data of two studies is given in Fig. 8.

There are several [bmim][PF₆]–CO₂ high-pressure vapor–liquid equilibrium data sets available in the literature. However, these sets differ from each other considerably in the values they report for similar conditions. The reason of differing solubility data reported may be due to the small amounts of water dissolved in the IL sample used. For example, Blanchard et al. [125] presented a solubility data of CO₂ in [bmim][PF₆] which is different than the data reported by the same group in 2001. In the first study, this group used [bmim][PF₆] which was saturated with water at 22 °C, containing 2.3 wt.% water. In the second study, they used [bmim][PF₆] which was dried to approximately 0.15 wt.% water. Drying of IL has a significant effect on the phase behavior with CO₂. Thus, Blanchard et al. [70] showed that the solubility of CO₂ in ILs was decreased in the presence of water. In Fig. 9, [bmim][PF₆]–CO₂ liquid phase compositions are given for dried and wet IL samples.

In order to observe the effect of water impurity in IL, phase behaviors of two IL samples (dry and wet) with CO₂ were compared. The effect of water impurity in IL is significant at 57 bar. For dried IL sample, the mole fraction of CO₂ is 0.54, whereas for the wet (water saturated) IL sample it is only 0.13. The effect of water in IL may be explained by CO₂-phobic nature of water. Even at high pressures, mutual solubilities of water and CO₂ are very low [126]. Another point is the formation of carbonic acid from the reaction of CO₂ with water that can result in a reduction of the aqueous phase pH to as little as 2.80 [127].

Rubero and Balderelli [128] investigated gas–liquid interface of imidazolium ILs using surface-sensitive vibrational spectroscopy sum frequency generation. The results indicated that when the IL is dry, the cation is oriented with the imidazolium ring parallel to the surface plane for both hydrophilic and hydrophobic ILs. But the cation reorients itself with respect to the surface for the hydrophobic liquid when water is added, while the orientation in the hydrophilic liquid is unaffected.

After the influence of water is noticed, researchers working on IL–CO₂ solubility and equilibrium have started to dry and degas all ILs under vacuum at room temperature for several days prior to use. After ILs are dried and degassed, the water contents are estimated by the Karl Fischer analysis before solubility data are taken. Measurements show that the most widely studied IL: [bmim][PF₆] absorbs a couple wt.% water when left to the atmosphere. The estimated water content of [bmim][PF₆] after drying was approximately 0.15 wt.% water as measured by Karl Fischer analysis [70].

A number of high and low-pressure [bmim][PF₆]–CO₂ solubility studies have appeared in the literature. Although consistent
results have been established for low-pressure solubility data of CO2 in [bmim][PF6], there are large discrepancies among high-pressure solubility data of several researchers [13,70,119–121]. These large solubility differences in the literature are most probably due to the differences in the purities of the ILs used.

Since the behaviors of IL–CO2 systems are different from other organic liquid–CO2 systems, full phase diagrams of IL–CO2 systems are investigated. Blanchard and co-workers [125] found two-phase immiscibility regions with three cloud point measurements of 1.31, 4.92 and 7.15 mole% IL mixtures with the balance being CO2. Although, these experiments were conducted with water-saturated ILs, qualitatively a similar behavior is expected with dried samples.

Blanchard et al. [70] gave a qualitative phase behavior of [bmim][PF6]–CO2 system over a wide pressure range. They noticed that the phase behavior where a large miscibility gap exists even at extremely high pressures. Blanchard et al. [70] reported and referred that as a complementary work, McHugh and co-workers studied [bmim][PF6]–CO2 phase behavior at higher pressures up to 3100 bar and found two distinct phases at all conditions. The existence of large immiscibility gap even at very high pressures is not expected for organic liquid–CO2 systems and the existence of two distinct phases is explained by the following discussion: At high-pressures density of pure CO2 phase increases but since the liquid phase does not expand, the two phases will never become identical and a mixture critical point will never be reached. Therefore, the IL–CO2 system remains as two phases even at very high pressures, although the CO2 solubility is quite high, the mixtures never become a single phase [70].

Anthony et al. [69] reported the solubilities and Henry’s constants of different gases (carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen, and nitrogen) in [bmim][PF6] and showed that CO2 has the highest solubility and strong interaction with [bmim][PF6]. The solubility data of CO2 in [bmim][PF6] is in good agreement with the published results of Blanchard et al. [70] although different techniques were used in these studies. Furthermore, Baltus et al. [68] reported that Henry’s constants for Kamps et al. [119] data are in reasonable agreement with those obtained by Anthony et al. [69].

Aki et al. [121] studied the high-pressure phase behavior of CO2 in imidazolium-based ILs and compared the phase behavior of the system [bmim][PF6]–CO2 with the other solubility data present in the literature. The solubility results of CO2 in [bmim][PF6] at 25 °C measured by Aki et al. [121] agreed remarkably well with the solubility results of Anthony et al. [69] at low pressures and with the solubility results of Kamps et al. [119]. Aki et al. [121] investigated the solubility of CO2 in [bmim][PF6] at 40 °C and compared the results with the previous studies of Kamps et al. [119], Blanchard et al. [70] and Liu et al. [120]. As expected the agreement between the data points is good at low pressures but the discrepancy is obvious at high pressures. Aki et al. [121] explained that in their previous work [70], they were not aware of the various impurities and degradation products that were present in the samples they used. Therefore, they attributed the difference between their study [121] and the previous study of the same group [70] to the purity of the IL.

At 40 °C and at all pressures, there is a very good agreement within the solubility values reported by Aki et al. [121] and Liu et al. [120]. However, this statement is not correct for the reported solubility data of Aki et al. [121] and Kamps et al. [119]. The results of two studies agree at low pressures, but at high pressures, there is a significant difference: At about 43 bar, the solubility of CO2 in [bmim][PF6] was measured as 0.43 (mole fraction) by Aki et al. [121], however, at the same point Kamps et al. [119] reported the solubility of CO2 as 0.38. By considering the studies mentioned above, it may thus be concluded that the solubility of CO2 in one of the most widely studied IL, [bmim][PF6], varies among different groups in the literature and is not a good agreement especially at higher pressures.

The solubility of CO2 in [bmim][PF6] was experimentally studied at 298.15 K and up to 1.0 MPa by Kim et al. [123]. A group contribution form of a non-random lattice–fluid model (GC-NLF) was applied to predict solubility of CO2 in [bmim][PF6]. They used the solubility data of Kamps et al. [119] for a wider pressure range for the group parameter determination. Comparisons of calculated solubility data with Kamps et al. data [119] for [bmim][PF6] demonstrated that the method applied is fairly accurate except for regions close to the critical conditions of CO2. Kim et al. [123] also compared the calculated values of solubility of CO2 in different ILs ([emim][PF6], [bmim][PF6], and [C6mim][PF6]) with the experimental solubility data reported by other groups for the same ILs. The agreements are generally good up to 10 MPa pressure, however, further comparisons for higher pressure shows some degree of discrepancy between the calculated solubility data of Kim et al. [123] and the experimental solubility data of Shariati and Peters [129,130].

Finally, Shariati and Peters [13] studied the comparison of the phase behavior of [bmim][PF6]–scCO2 system with the other studies present in the literature. The solubility of CO2 in [bmim][PF6] was determined by measuring the bubble point pressure of the binary system at different temperatures for several isopleths and pressures up to 97 MPa. The solubility data of CO2 in [bmim][PF6] at 323.15 K was compared with that of Blanchard et al. [70] and Anthony et al. [71] and the results of Shariati and Peters [13] were in a good agreement with those of Anthony et al. [71]. The solubility data taken at 333.15 K was compared with that of Blanchard et al. [70], Kamps et al. [119], Liu et al. [120]. Although the experimental methods were completely different, there is also a good agreement between the results of Shariati and Peters [13] and Kamps et al. [119] at a temperature of 333.15 K. The solubility data of Blanchard et al. [70] and Liu et al. [120] show greater deviations from the data of Shariati and Peters [13] especially at higher pressures. Shariati and Peters [13] reported the existence of the three-phase equilibrium liquid–liquid–vapor (LLV). As the other studies demonstrated, this study also indicated that CO2 has a high solubility in [bmim][PF6] and there is a linear relationship between the alkyl chain length and the solubility of CO2.
7.1.2. Other IL–CO2 systems

High-pressure phase behavior of different types of ILs are similar to that of [bmim][PF6]. Blanchard et al. [70] investigated the high-pressure phase behavior of CO2 with six different ILs: 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]), 1-n-octyl-3-methylimidazolium hexafluorophosphate ([C8-mim][PF6]), 1-n-octyl-3-methylimidazolium tetrafluoroborate ([C8-mim][BF4]), 1-n-butyl-3-methylimidazolium nitrate ([bmim][NO3]), 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO4]), and N-butylpyridinium tetrafluoroborate ([N-bupy][BF4]). They investigated the solubility of CO2 in different ILs at 40, 50, 60°C and pressures up to 93 bar. The focus of the work was to develop an insight into the physical interaction between CO2 and ILs with different cation–anion configurations. The solubility of CO2 in the IL-rich phase was greatest for ILs with fluorinated anions, following the trend of [bmim][BF4] and [C8-mim][BF4] > [C8-mim][PF6] > [N-bupy][BF4] > [bmim][NO3] > [emim][EtSO4] [70]. The solubility of CO2 was found to be greatest in ILs with PF6−, anion and the IL that exhibited the lowest solubility of CO2 was [emim][EtSO4].

The solubility of CO2 in ILs increases with increasing pressure but the exact amount of CO2 dissolved in the liquid phase varies significantly. In the study of Blanchard et al. [70], it is found that at 70 bar the solubility of CO2 in [emim][EtSO4] was 0.36 (mole fraction) whereas, it was 0.63 in [C8-mim][PF6]. Although there are some numerical differences in the mole fraction of CO2 dissolved, the general trend of the phase behavior is nearly identical for all ILs. The solubility of CO2 in the IL-rich phase changes slightly with the temperature as in the case of [bmim][PF6]–CO2 system. Since the qualitative phase behavior of almost all ILs seems similar, it can easily be concluded that scCO2 can be used to recover solutes not only from [bmim][PF6] but also from all kind of ILs.

In order to understand the effect of the anion on the phase behavior of IL–CO2 systems, two pairs of ILs with the same cations were compared: [C8-mim][BF4]–[C8-mim][BF4] and [bmim][PF6]–[bmim][NO3]. Changing the anion from [PF6]− to [BF4]− in the [C8-mim] salts, results in an approximately 8% decrease in CO2 solubility at 40°C over the range of pressures studied by Blanchard et al. [70]. The solubility of CO2 in [bmim][NO3] is about 25% less than in [bmim][PF6]. Experimental and molecular simulation studies found that the anions of IL dominate the interaction with CO2, with the cation playing a secondary role. Cadena et al. [122] pointed out that the changes in the imidazolium cation involving alkyl groups have relatively little influence on the solubility of CO2 in IL.

[bmim][BF4] is one of the popular ILs which has been very widely used in most of the studies; Husson-Borg et al. [131] reported the solubility of CO2 in [bmim][BF4] as a function of temperature between 303 and 343 K and at atmospheric pressure. This group used a new type of experimental apparatus based on a saturation method. The equilibrium cell is specially designed for viscous solvents like the IL, and an appropriate gas–liquid contact is obtained by good agitation. Kroon et al. [132] studied the phase behavior of different IL-supercritical fluid systems including [bmim][BF4]. They investigated the phase behavior of [bmim][PF6]–CO2 binary system experimentally and reported its bubble point pressures for CO2 concentrations between 10.22 and 60.17 mole% and in a temperatures range of 278.47–368.22 K. They found that CO2 has a high solubility at lower pressures, but the solubility decreases dramatically at higher pressures. The experimental results for the [bmim][BF4]–CO2 system were compared with the available phase behavior data of the binary system 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF4])–CO2 [133] to investigate the effect of the alkyl group length on the phase behavior. The results showed that a larger alkyl group lead to lower bubble-point pressures and, therefore, to higher solubilities of CO2 in the imidazolium-based ionic liquid. Thus, CO2 was more soluble in [hmim][BF4] than in [bmim][BF4].

Shariati and Peters [129] studied the phase behavior of binary system [emim][PF6]–CO2 experimentally by measuring its bubble point pressures at temperatures and pressure ranges of 308.14–366.03 K and 1.49–97.10 MPa, and compared it with [bmim][PF6]–CO2 system to understand the effect of the length of alkyl chain on the solubility of CO2. The solubility of CO2 in [bmim][PF6] is higher than in [emim][PF6]. Since the butyl group in [bmim][PF6] is bulkier than the ethyl group in [emim][PF6], Shariati and Peters [129] emphasized that CO2 can dissolve better in [bmim][PF6] than in [emim][PF6], the latter component being denser. Moreover, it was observed that the experimentally determined phase behavior of the [emim][PF6]–CO2 is similar to the phase behavior of [bmim][PF6]–CO2 at 333.15 K.

Aki et al. [121] also presented the solubility of CO2 in ten different imidazolium-based ILs at 25, 40, and 60°C and pressures to 150 bar. They concluded that the solubility of CO2 in imidazolium-based ILs increases with increasing pressure and decreases with increasing temperature for all the ILs investigated. Furthermore, Aki et al. [121] investigated the influence of the different anions, namely; dicyanamide ([DCA]), nitrate ([NO3]), tetrafluoroborate ([BF4]), hexafluorophosphate ([PF6]), trifluoromethanesulfonate ([TfO]), bis(trifluoromethylsulfonyl) imide ([Tf2N]), and tris(trifluoromethylsulfonyl)methide ([methide]). The results of their study showed that the solubility of CO2 is strongly dependent on the choice of anion. Solubility measurements of Anthony et al. [69] and Cadena et al. [122]; spectroscopic studies of Kazarian et al. [134] also all showed that the solubility of CO2 in ILs depend on the anion, especially the interaction between the anion of the IL and CO2.

CO2 is the least soluble in the two ILs with non-fluorinated anions, [NO3] and [DCA], and it has the highest solubility in ILs with anions containing fluoroalkyl groups, [TfO], [Tf2N], and [methide]. Aki et al. [121] attributed the high solubility of CO2 in ILs to the anions containing fluoroalkyl groups as a result of favorable interactions between CO2 and the fluoroalkyl substituents on the anion since fluoroalkyl groups are known as CO2-philic ones [135–137].

Aki et al. [121] also compared the solubility of CO2 in [bmim][Tf2N], [hmim][Tf2N], and [omim][Tf2N] at 25, 40, and
60°C to investigate the influence of cation alkyl chain length. The solubility of CO2 increases with an increase in the alkyl chain length at all pressures, with the increase being more apparent at higher pressures. This result of Aki et al. [121] is consistent with the results of previous studies of Shariati and Peters [129,130]. Furthermore, Blanchard et al. [70] reported that the CO2 solubility increases when the alkyl chain length was increased from butyl to octyl for ILs containing [PF6]. It is known that the densities of the imidazolium-based ILs decrease as the alkyl chain length increases [49,138]. Therefore, imidazolium-based ILs with longer alkyl chains have greater free volume and thus greater solubility of CO2 is expected in these ILs. Therefore, the higher solubility of CO2 in ILs with longer cation alkyl chains may be attributed to the entropic rather than enthalpic arguments [121]. Finally, it may be concluded that it is possible to increase the solubility of CO2 in ILs by increasing the alkyl chain length on the cation.

Constantini et al. [133] investigated the phase behavior of a binary mixture of 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF4])–scCO2 system and compared it with the experimental data of the binary system of 1-hexyl-3-methylimidazolium hexafluoroborate ([hmim][PF6])–scCO2 system, in order to demonstrate the anion effect. Although the phase behaviors of the binary systems are similar, the solubility of the scCO2 is found to be higher in [hmim][PF6] than in [hmim][BF4]. This higher solubility may be explained with the greater interaction between CO2 and the [PF6] anion, although the former is denser than the latter [133].

In another study [139], the high-pressure phase behavior of the binary system 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF4])–CO2 was studied in the liquid-phase CO2 mole fraction range 0.1–0.75, and in the pressure and temperature range of 0.1–100 MPa and 303–363 K. They compared their experimental data with the data given by Blanchard et al. [70]. Although there was a discrepancy between two studies for CO2 mole fractions higher than 0.6, they both suggested a peculiar behavior of a rapid pressure increase at higher CO2 mole fractions [139]. Kroon et al. [140] presented the phase behavior of several IL–CO2 binary systems experimentally, and finally developed an equation of state (EoS) to predict the phase behavior of IL–CO2 systems based on the truncated perturbed chain polar statistical associating fluid theory (tPC-PSAFT) EoS. The EoS was used to describe the CO2 solubility in several 1-alkyl-3-methylimidazolium-based ionic liquids with different alkyl chain lengths within a pressure and CO2 mole fraction range of 0–100 MPa and 0–75%, respectively. The binary interaction parameter was fitted to V–L equilibrium data.

In general when a gas is dissolved in a liquid phase, dilation of the liquid occurs. ILs show only slight dilations in volume with CO2 dissolution. This behavior is different than normal liquid–CO2 systems. In fact, the dissolution of CO2 in liquids to expand them and reduce their solvent strength is a well-known phenomenon and it is the basis of gas anti-solvent (GAS) process to precipitate solutes from liquids [141]. However, ILs do not follow this trend due to the strong Coulombic forces associated with the ionic nature of ILs. The lack of expansion of ILs seems to derive from the fact that dissolved CO2 does not greatly affect the strength of interionic interactions in IL. Therefore, the IL–CO2 system is extremely different from other organic liquid–CO2 systems with the large immiscibility region and lack of dilation of the liquid phase [70].

Although there are not so many available studies concerning the IL/SCF other than CO2 systems, for the completeness of the material they must be mentioned. Shariati and Peters [142] investigated the high-pressure phase behavior of [emim][PF6]–supercritical fluoroform, the experimental conditions and the results of this study is given on Table 3.

7.2. IL solubility in CO2

The majority of the research focus on the solubility of CO2 in IL, on the other hand the concentration of IL in CO2-rich phase is also important. A dynamic apparatus with a high-pressure cell, was used to measure the solubility of [bmim][PF6] in the CO2-rich phase [70]. The solubility of [bmim][PF6] in CO2 was determined at 40°C and 137.9 bar by flowing 0.5866 mole of CO2 through a cartridge loaded with [bmim][PF6]. UV–visible analysis gave no appreciable IL absorption peak, indicating [bmim][PF6] solubility of less than 5 × 10−7 (mole fraction of [bmim][PF6]) in the CO2 phase. Due to the fact that no measurable IL dissolves in CO2, a solute dissolved in an IL can be easily recovered with scCO2 without any cross contamination. The lack of solubility of IL in the CO2 phase can be attributed to two reasons: extremely low vapor pressure of IL and the inability of CO2 to adequately solvate ions in the gaseous phase.

Although the solubility of IL in scCO2 is extremely low and not measurable, in industrial applications, the scCO2 phase may contain some other components such as reactants, products which may act as cosolvents to enhance the ability of scCO2 to dissolve IL significantly. In this case, the amount of IL dissolved in CO2-rich phase may not be negligible under some conditions. In order to decide on the conditions to avoid cross contamination, solubility of IL in scCO2/organic compound mixtures must be known. Wu et al. [143] conducted the first study in the literature to observe the effect of organic compounds in scCO2 on the solubility of an IL in CO2 phase. The solubility of [bmim][PF6] in scCO2, and in scCO2–ethanol, scCO2–acetone, scCO2–n-hexane mixtures was investigated quantitatively. The solubility of IL in scCO2 is extremely low as the earlier studies suggested, however by addition of ethanol and acetone, the solubility of IL increases dramatically as the concentration of the organic compounds in scCO2 exceeds 10 mole%. This enhancement of the IL solubility by addition of ethanol and acetone results mainly from strong interaction of the two compounds with the IL due to their strong polarity. The polarity of acetone is stronger than ethanol; therefore, the solubility of IL is higher in the scCO2–acetone system than in the scCO2–ethanol system. Since n-hexane is a nonpolar substance its influence on the solubility of IL in scCO2 phase is very limited. A further study of Wu et al. [144] also showed that the ability of cosolvents to increase the solubility of ILs ([bmim][PF6] and [bmim][BF4]) in scCO2 follows the order: acetonitrile > acetone > methanol > ethanol > n-hexane. This order is same with the order of dipole moments of cosolvents. With this
discussion, it is clear that the polarity of the organic compound is a dominant factor in influencing solubility. With this study Wu et al. [144] emphasized that the amount of IL dissolved in scCO2-rich phase may be significant if the system contains sufficiently polar organic compounds in sufficient concentrations. Table 4 shows the studies of Blanchard et al. [70], Wu et al. [143] and Wu et al. [144], the components of their systems, experimental conditions and basic results.

The phase behavior of the IL–CO2–methanol system and the viscosity of the mixtures were studied previously by Liu et al. [120] at different conditions. The phase behavior of IL–CO2–water system was investigated by Zhang et al. [145] and finally this group studied the phase behavior of [bmim][PF6]–CO2–acetone system in detail at 313.15 K over a wide pressure range. Zhang et al. [146] determined the distribution coefficients of the components between different phases and found that CO2 distribution coefficient decreases with increasing pressure while the acetone distribution coefficient increased with pressure.

### 7.3. IL–CO2 interaction at the molecular level

An in situ attenuated total reflectance–infra red (ATR–IR) study of CO2 dissolved in two ILs ([bmim][PF6] and [bmim][BF4]) at high pressures has demonstrated the effects of anionic species of the ILs on the molecular state of the dissolved CO2. Kazarian et al. [147] showed that CO2 forms weak Lewis acid–base complexes with the anions in [bmim][PF6] and [bmim][BF4]. Furthermore, they demonstrated that this interaction is stronger with [bmim][BF4], BF4− acts as a stronger Lewis base towards CO2 than PF6−. In addition to this, as the size of anion increases the strength of interaction decreases. However, the solubility data of various group indicated that CO2 has a higher solubility in [bmim][PF6] than in [bmim][BF4]. Thus, the strength of these interactions cannot be solely responsible for the solubility of CO2 in these ILs, and presumably, a free volume contribution in IL plays a significant role [148]. The strength of the anion–cation interactions in IL affects the available free volume and one can expect that a weaker interacting anion leads to more free volume being available.

ILs are generally distinguished with their low melting points. Another in situ ATR–IR spectroscopic study of Kazarian et al. [134] showed that high-pressure CO2 reduces the melting temperature of ILs. This possibility of reducing melting temperature of ILs further under high pressure CO2 provides a new opportunity to use ILs as solvents at milder temperatures. Kazarian et al. [134] investigated the effect of CO2 pressure on the phase behavior of 1-hexadecyl-3-imidazolium hexafluorophosphate. The data presented indicated that 70 bar CO2 reduces the melting point of this IL from 75 to 50 °C. This result was assigned to a weak Lewis acid–base type interaction between anion and CO2, with the P–F bonds perpendicular to O=C=C axis thereby reducing the rather stronger interactions between the P–F bonds and the cations. CO2 disrupts the cation–anion and the tail-tail interactions in IL rather than simply playing an impurity role in the mechanism of induced melting. Preliminary results obtained by Kazarian et al. [134] also indicated that melting temperatures of other analogous ILs decrease by high pressure CO2 allowing their use in many applications at mild temperatures.

### 7.4. Solute recovery from ILs with scCO2

Researchers found that nonvolatile organic compounds can be extracted from ILs using scCO2, which is widely used to extract large organic compounds with minimal pollution. Blanchard et al. [125] showed that CO2 can be used to extract naphthalene, a low volatility model solute, from an IL. They synthesized [bmim][PF6] which was stable in the presence of water and oxygen. The model compound naphthalene was readily soluble in [bmim][PF6] (maximum solubility of 0.30 mole fraction at 40 °C) and in CO2. Their study investigated the phase behavior of [bmim][PF6] with CO2, as well as with naphthalene and finally that of the [bmim][PF6]–CO2–naphthalene ternary system. The results showed that CO2-rich phase was not significantly contaminated by IL, as would be expected during contact of CO2 with any conventional organic solvent. Blanchard et al.

### Table 4

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Findings</th>
<th>Reference</th>
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<tr>
<td>[bmim][PF6]–CO2</td>
<td>40 °C</td>
<td>137.9 bar</td>
<td>The solubility of [bmim][PF6] in scCO2 is extremely low scCO2 may be used to recover solutes dissolved in IL without any cross contamination</td>
<td>[70]</td>
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<tr>
<td>[bmim][PF6]–CO2–ethanol</td>
<td>40 and 55 °C</td>
<td>12–15 MPa</td>
<td>By addition of ethanol and acetone, the solubility of the IL in scCO2 phase enhances</td>
<td>[143]</td>
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<tr>
<td>[bmim][PF6]–CO2–acetonitrile</td>
<td>40 °C</td>
<td>15 MPa</td>
<td>By the addition of organic cosolvents, the solubility of ILs in scCO2 phase may be enhanced significantly</td>
<td>[144]</td>
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<td>[bmim][PF6]–CO2–methanol</td>
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[125] demonstrated that CO₂ is highly soluble in [bmim][PF₆] reaching a mole fraction of 0.6 at 8 MPa. After extracting IL with CO₂ at 13.8 MPa and 40 °C there was no detectable [bmim][PF₆] in the extract, indicating that the solubility is less than 10⁻⁵ mole fraction. In contrast to this result, a mixture of CO₂ with conventional organic liquid results in significant solubility of the liquid in the CO₂ phase. A mixture of 0.12 mole fraction naphthalene in [bmim][PF₆] was extracted with CO₂ at 13.8 MPa and 40 °C with recoveries of 94–96% and therefore it was concluded that it is possible to quantitatively extract an organic solute having a reasonable molecular weight from IL using scCO₂ without any cross contamination. Furthermore, the dissolution of scCO₂ in IL was completely reversible and pure IL remained after the extraction of naphthalene and depressurization [125].

The experimental work of Blanchard and Brennecke [118], which showed that a wide variety of solutes can be extracted from [bmim][PF₆] with scCO₂, with recovery rates greater than 95%, provided a significant step to visualize the partnership established by the IL–CO₂ system. One of the essential problems of ILs, namely product recovery, was solved by applying the SCFE technique. Hexane and benzene were chosen as the roots to which numerous substituents groups were added to explore the effect of chemical structure on the solubility and extractability of an organic solute in and from an IL. The substituent groups represented were halogen, alcohol, ether, amide, ketone, carboxylic acid, ester, and aldehyde with a wide range of polarity. The extraction experiments were conducted at 40 °C and 138 bar. The authors noted that for some organic solutes, scCO₂ extraction achieved greater than 98% recoveries before the extraction test was terminated. These high recovery rates clearly indicated that although the ionic nature of IL might lead to an interaction with solute, it did not limit the extent of reaction. Benzene and chlorobenzene which exhibited phase immiscibility with [bmim][PF₆] required the least amount of CO₂ for recovery. Phenols, benzoic acid and benzamide which are solids at room temperature, required the largest amount of CO₂. Figs. 10 and 11 illustrate % recovery of solutes as a function of molar ratio of CO₂ passed through the extractor to organic solute loaded in the reactor (solute dipole moments are also given in these figures in terms of Debye). In this paper they showed that there was a relation between the dipole moments of solutes and the amount of CO₂ required for extraction, concluding that the organics with a dipole moment of zero (such as benzene, hexane, cyclohexane, etc.) are easily extracted compared to solutes with nonzero dipole moments. Fig. 12 illustrates the number of CO₂ per mole of organic solute as a function of dipole moment.

Studies on the solubilities of organics in [bmim][PF₆] were carried out under ambient conditions, 22 °C and 0.98 bar [118], where IL–solute mixtures were stirred in closed containers to avoid contamination with air and water vapor. Their results demonstrated that organics with the potential for strong intermolecular interactions, those with a large dipole moment for example, generally exhibited complete miscibility or a large degree of solubility in [bmim][PF₆]. Solubilities of the solid organic solutes were considerably less than the solubilities of the liquid organics, with the exception of the phenol. The authors

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Fig. 10. Extraction of aromatic solutes from [bmim][PF₆] with scCO₂ at 40 °C and 138 bar. (Reprinted with permission from [118]. Copyright 2001 American Chemical Society)

Fig. 11. Extraction of aliphatic solutes from [bmim][PF₆] with scCO₂ at 40 °C and 138 bar. (Reprinted with permission from [118]. Copyright 2001 American Chemical Society)

Fig. 12. Effect of solute dipole moment on ease of extraction of [bmim][PF₆] with scCO₂ at 40 °C and 138 bar. (Reprinted with permission from [118]. Copyright 2001 American Chemical Society)
concluded that the solubilities of the benzene-based organics were significantly greater than those of their hexane-based counterparts. Solubility measurement results indicated that aromatic compounds are more soluble in [bmim][PF₆] than in non-aromatic compounds of equivalent molecular weight and polarity.

Distribution coefficient (K), may be defined as the ratio of solute mole fractions in the supercritical and in the IL phases, respectively. Since ILs do not dissolve in scCO₂ appreciably, supercritical phase is essentially CO₂ and organic solute. The distribution coefficient is an important thermodynamic property to comprehend the IL–scCO₂–solute systems. Theoretically, one can anticipate the trend of distribution coefficient between the IL and the scCO₂ phases by considering the volatility and polarity characteristics of the solute. For example, a solute with high volatility and low polarity will have a large affinity for CO₂, whereas a solute with high polarity and aromaticity will have a large affinity for the IL-rich liquid phase. Therefore, solutes with high polarities give a small K value due to high affinity for IL and low affinity for CO₂. Conversely, nonpolar solutes give large K values as a result of high affinity for CO₂. With this discussion, it is clear that the compounds that have high affinity for CO₂ can be more easily extracted from the IL mixture.

The phase behaviors of the organic solute–CO₂ binary systems also affect the ease of extraction of a compound from ILs with scCO₂. Investigating the liquid phase data at low pressures, a measure of affinity of compounds for CO₂ was determined, and also that compounds in which CO₂ readily dissolves at low pressures have a greater attraction for CO₂ [118]. Furthermore, the molar ratio of CO₂ to solute for 95% recovery is determined as 1:1.4 from an IL saturated aqueous solution at 293 K and at a CO₂ pressure of 4.9 MPa.

The result of the mentioned studies presented that organic compound–IL–scCO₂ mixture has a complex phase behavior. According to the results of their research Scurto et al. [151] emphasized that during the IL–scCO₂ reaction studies in which larger amounts of organic reactant and products are present, one must be aware of the possible formation of the additional liquid phases that might contain only part of the components necessary for the desired reaction. After showing ILs could be recovered from methanol and water using CO₂-induced separation, the same research group [153] investigated the factors that control the vapor–liquid–liquid equilibrium in IL–organic compound–CO₂ ternary systems via studying on several homogeneous IL–organic compound mixtures. The experiments were conducted at 40 °C. The results showed that the lowest critical endpoint pressure (LCEP) was dependent on the choice of both organic, IL and the initial concentration of IL in the organic. The K-point pressure was however independent of the type of IL, was identical with the organic compound–CO₂ mixture critical point. Najdanovic-Visak et al. [154] investigated the vapor–liquid equilibrium of ternary (1-butanol–water–CO₂) and quaternary ([C₄mim][NTf₂]–1-butanol–water–CO₂) systems. The demixing pressures of both mixtures were strongly controlled by the water concentration.

The studies concerning the solute recovery from ILs by scCO₂, the system components, experimental conditions, major results of the studies and related references are given in Table 5.

### 7.5. Other applications of IL–scCO₂ systems

Brennecke and Maginn [8] discussed the potential industrial applications of ILs in many areas such as catalytic reactions, liquid–liquid extractions, gas separations etc. After the IL–scCO₂ systems and the advantages of these systems are realized, a number of studies have been done for IL–CO₂ biphasic systems: It is shown that a desired solute may be extracted from an IL using scCO₂ without any cross contamination [118,125]. The use of scCO₂ to separate ILs from their organic solvents [151]; the addition of CO₂ to separate hydrophobic and hydrophilic imidazolium-based ILs from aqueous solutions [152] have all been important applications of IL–scCO₂ systems. Dzyuba and Bartsch [155] demonstrated the recent applications of room temperature IL–scCO₂ systems in metal catalyzed organic reactions and enzyme-catalyzed transformations. The solubility or stability of organometallic or enzymatic catalysts in ILs and their negligible solubility in scCO₂ is the basic advantage of IL–scCO₂ systems.

Several groups have studied the IL–scCO₂ reaction systems [156–168]. In these studies, mostly IL was used as reaction media and scCO₂ was used as transport media for reactants and products. Cole-Hamilton et al. [169] summarized the continuous flow homogeneous catalysis using IL–scCO₂ biphasic systems in detail according reaction types. Also, Gordon and Leitner [170] mentioned some of IL–scCO₂ biphasic reaction systems. In the following paragraphs, IL–scCO₂ biphasic reaction systems are summarized.
Sellin et al. [156] and Webb et al. [157] studied the hydroformylation of alkenes in IL–scCO\(_2\) biphasic reaction media and described the continuous flow homogeneous catalysis in IL–scCO\(_2\) biphasic system. They dissolved the catalyst in ionic liquid and used scCO\(_2\) as the transport medium for the substrates and products. In Sellin et al. [156], they demonstrated the hydroformylation of several alkenes such as 1-hexene, 1-nonene and 1-octene in IL–scCO\(_2\) biphasic mixture. First, the hydroformylation of 1-hexene was studied using triphenylphosphite as the rhodium-based ligand ([Rh\(_2\)(OAc)\(_4\)]/P(OPh)\(_3\)) in [bmim][PF\(_6\)] using scCO\(_2\). The hydroformylation of 1-hexene was also performed in [bmim][PF\(_6\)] without scCO\(_2\). The results showed that addition of scCO\(_2\) to the reaction mixture lowers the conversion from >99–40%, but the selectivity and linear to branched (l:b) ratio were enhanced from 15.7 to 83.5% and 2.4 to 6.1, respectively. The success of this system encouraged the authors to carry out similar reactions of 1-hexene and 1-nonene with repetitive uses of the same catalyst to search for the possibility of continuous flow homogeneous catalysis. They found that the catalyst retained its activity and selectivity for only three to three runs, so in order to eliminate this drawback, the ligand–catalyst system was changed. [Ph\(_2\)P(C\(_6\)H\(_4\)SO\(_3\))]–[bmim] was used together with [Rh\(_2\)(OAc)\(_4\)] as the catalyst precursor for the hydroformylation of 1-nonene in the ([bmim][PF\(_6\])–scCO\(_2\) biphasic system. The products were flushed from the reactor with scCO\(_2\). The activity of this catalyst system remained high for 12 runs with an acceptable l:b ratio. However, after the ninth run Rh leaching became important which was attributed to ligand oxidation. Contamination with air during the many openings of the reactor may cause the oxidation, which will be eliminated during continuous flow. Finally, Sellin et al. [156] demonstrated the continuous hydroformylation of 1-octene using [PhP(C\(_6\)H\(_4\)SO\(_3\))]–[pmim] and [Rh\(_2\)(OAc)\(_4\)] dissolved in [bmim][PF\(_6\)]. The reactants and the products were transported into and out of the reaction medium via scCO\(_2\). The total pressure, temperature and reaction time were 200 bar, 100 °C and 33 h. The results showed that the catalyst was stable at least between 8 and 10 h reaction time, no ligand oxidation occurred and the l:b ratio of the product aldehydes was 3.1. In another study, Webb et al. [157] investigated the hydroformylation 1-dodecene which was representative for hydroformylation of relatively low volatility alkenes. The reactions were catalyzed by either Rh/[pmim][Ph\(_2\)P(3-C\(_6\)H\(_4\)SO\(_3\))] or Rh/[pmim][TPPMS]. The latter one was used for its easiness in crystallization and purification. They performed optimization reactions in order to obtain higher rates. They investigated the effect of the ionic liquid, substrate flow rate, temperature, gas composition on the rate of hydroformylation of 1-octene. Among several ionic liquids used ([bmim][PF\(_6\]), [bmim][NTf\(_2\]), [octmim][PF\(_6\]), [octmim][NTf\(_2\]), [decimim][NTf\(_2\]), [octmim]NTf\(_2\) was found to be the most effective in terms of high conversion rates attained (>80%).
The authors found that the catalyst turnover frequency (TOF), which indicates productivity, could be >500 h⁻¹ as the substrate (1-octene) flow rate was increased (>0.3 mL/min) at 200 bar and 100 °C. They concluded that continuous flow homogeneous catalysis in IL–scCO₂ biphasic system can be used for hydroformylation of long chain alkenes at rates comparable with the ones found in commercial systems. In the latest study conducted by Cole-Hamilton and co-workers [158] on hydroformylation of alkenes, they achieved rapid hydroformylation of 1-octene (rates up to 800 h⁻¹) with the catalyst remaining stable for at least 40 h and with very low rhodium leaching levels (0.5 ppm). A new system, in which the substrate, reacting gases and products dissolved in scCO₂ and were flowing over a fixed bed "supported ionic liquid phase (SILP)" catalyst, was introduced. The reactants in scCO₂ (1-octene, CO and H₂) flowed upwards through a tubular reactor containing a catalyst composed of [prmim][Ph₃P(3-C₆H₄SO₃)], [Rh(acac)(CO)₂] and [octmim][TF₂N] supported on silica gel at 100 °C, and 100 bar. The authors claimed that this new system provided excellent diffusion of the substrate and gases to the catalyst surface, excellent solubility of the substrates and gases within the supported ionic liquid and extraction of heavy products that might otherwise foul the catalyst by filling the pores.

There were two other studies on SILP catalysis [171,172], but both studies were conducted in batch mode. Wang et al. [171] described the synthesis of cyclic carbonates from CO₂ and epoxides over silica-supported quaternary ammoniumsalts and Ciriminna et al. [172] studied the aerobic oxidation of alcohols over a perruthenate catalyst.

Brown et al. [159] studied the asymmetric hydrogenation of tiglic acid catalyzed by Ru(O₂CMe)₂(R–tolBINAP) in [bmim]PF₆ with addition of water as cosolvent. In this study, scCO₂ was not involved in the reaction, but it was used to recover the products from the IL after the reaction time was over. The results were evaluated in terms of enantioselectivity and conversion. The catalyst/ionic liquid solution was reused repeatedly (five cycles) without significant loss of selectivity or conversion. In another work of the same group [160], a number of different solvents were studied in order to evaluate the most effective system for the enantioselective hydrogenation of α,β-unsaturated acids. Different solvent systems comprised scCO₂, different ILs, ILs with cosolvents and also CO₂ expanded ionic liquids. They studied two types of substrates, namely class I (atropic acid) and class II (tiglic acid) substrates. Class I substrates were hydrogenated in high enantioselectivity at high H₂ concentration whereas Class II substrates were hydrogenated in high enantioselectivity at low H₂ concentration. For both substrates, Ru(O₂CMe)₂(R–tolBINAP) was used as the catalyst. Atropic acid was hydrogenated with the highest enantioselectivity (92%) in methanol (50 bar H₂ pressure). Lower enantioselectivity values were obtained for reactions in ILs ([bmim][PF₆]—32%, [bmim][BF₄]—15%, [emim][O₂SCF₃]—25%, [emim][N(O₂SCF₃)₂]—31%, [dmpim][N(O₂SCF₃)₂]—39%) and IL–cosolvent systems ([bmim][PF₆]–toluene—19%, [bmim][PF₆]–PrOH—33%, [bmim][PF₆]–MeOH—54%) at 50 bar H₂ pressure. [bmim][PF₆], [bmim][PF₆]–toluene, [bmim][PF₆]–PrOH, [bmim][PF₆]–MeOH systems were expanded by CO₂ (50 bar CO₂). Expansion caused increases in enantioselectivity consistent with greater H₂ solubility and mass transfer rate in all mediums except for [bmim][PF₆]–toluene. Tiglic acid was hydrogenated with the highest enantioselectivity (95%) in [emim]N(O₂SCF₃)₂ (5 bar H₂). Reasonably high enantioselectivity values were also obtained for other ionic liquids, as the authors expected, because of low H₂ concentration ([dmpim][N(O₂SCF₃)₂]—93%, [bmim][PF₆]—93%, [mbpy][BF₄]—88%, [bmim][BF₄]—88%, [emim][O₂SCF₃]—84%). IL–cosolvent systems ([bmim][PF₆]–toluene, [bmim][PF₆]–PrOH) were less selective than hydrogenation in IL ([bmim][PF₆]) alone. Tiglic acid hydrogenations were also conducted in [bmim][PF₆], [bmim][PF₆]–toluene, [bmim][PF₆]–PrOH expanded systems. In these CO₂ (70–bar) expanded systems, decreases in enantioselectivity were observed when compared to non-expanded systems. The decrease in enantioselectivity for [bmim][PF₆] system was from 93% (non-expanded) to 85% (expanded).

Another example of hydrogenation reaction in IL–scCO₂ biphasic system was reported by Liu et al. [161]. IL phase was used to immobilize the transition metal catalys, and scCO₂ phase was used to recover the products. They examined the hydrogenation of 1-decene and cyclohexene using Wilkinson’s catalyst RhCl₂(PPh₃)₂, and hydrogenation of carbon dioxide in the presence of dialkylamines to form N,N-dialkyldiformamides using RuCl₂(dppe)₂ in [bmim][PF₆]–scCO₂ biphasic system. 98% conversion was attained for hydrogenation of 1-decane at 48 bar H₂ and 207 bar total pressure (TOF: 410 h⁻¹) at the end of 1 h reaction time. Hydrogenation of cyclohexene under the same experimental conditions mentioned above proceeded more slowly (82% conversion after 2 h, 96% conversion after 3 h). They also performed four repetitive batch runs for hydrogenation of 1-decene, and demonstrated the efficient catalyst recycling via immobilization in ionic liquid. The hydrogenation of 1-decane and cyclohexene were also done with [bmim][PF₆]–n-hexane biphasic system. The results showed that there was no reactivity advantage for CO₂ over n-hexane for simple hydrogenation reactions. The conversion and selectivity were much higher for hydrogenation of carbon dioxide in [bmim][PF₆]–scCO₂ biphasic medium starting with the di-n-propylformamide (80 °C, 276 bar, 5 h), when they were compared to the conversion and selectivity values obtained only in scCO₂ for less bulky diethyl-lamine and n-propylamine.

Bössmann et al. [162] also utilized the benefits of IL/CO₂ biphasic system to immobilize the organometallic catalyst in IL phase and recover the product without harming the catalyst. They investigated the continuous flow system for the hydrovinylnation of styrene with Wilke’s catalyst in IL/CO₂ biphasic system. They initially identified the suitable ILs that would allow the activation of the catalyst. It was found that the activation strongly depended on the IL’s anion type. The reaction conversion rates for the anions BARF (BARF: tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), Al[ Oc(CF₃)₂]₃Ph₄, TF₂N and BF₄ were 100, 90.5, 69.9 and 39.6, respectively for [emim] cation. It was also noted that the activation of the catalyst was not just a simple anion-exchange reaction, and the specific environment of the ionic solvent sys-
tem seemed to activate the catalyst. When [emim] and [4-mpb] (4-mpb: 1-n-butyl-4-methylpyridinium) were used as different cations with the same anion, it was reported that at comparable conversions, higher enantioselectivity values were found with [4-mpb][BF₄] and [4-mpb][Tf₂N] than the corresponding [emim] salts. The continuous flow styrene hydrovinylation was conducted in [emim][Tf₂N]–scCO₂ at 80 bar. The catalyst was stable over a reaction time of 61 h and enantioselectivity decreased slightly at that period, while products were extracted with compressed CO₂. Tkatchenko et al. [163] studied the palladium catalyzed dimerization of methyl methacrylate at 83 °C and 200 bar in [bmim][BF₄]–scCO₂ biphasic system. The selectivity (>98%) was identical to that of the monobasic system. The turnover frequency and turnover numbers were comparable for both monophasic and biphasic systems, increasing with increasing substrate to palladium ratios in the IL phase. They concluded that, as the CO₂-rich phase acted as a substrate and product reservoir, there was a possibility for the reaction to be conducted under continuous feed and product recovery conditions with greener solvents.

Hou et al. [164] investigated the oxidation of 1-hexene by molecular oxygen in [bmim][BF₆]–scCO₂ biphasic system as well as in [bmim][BF₆], scCO₂, and in the absence of solvent with catalysts PdCl₂ and CuCl₂. The results showed that the selectivity to the desired product 2-hexanone was much higher when the reaction was done in [bmim][BF₆]–scCO₂ biphasic system (125 bar, 333.2 K and 17 h of reaction time). Additionally, the catalyst was more stable in biphasic system than it was in scCO₂ only. Kawanami et al. [165] performed the chemical fixation of CO₂ to cyclic carbonates in a IL–scCO₂ biphasic system. They reported that synthesis of propylene carbonate from propylene oxide and carbon dioxide in [emim][BF₄]–scCO₂ biphasic system (14 MPa, 100 °C) was achieved with nearly 100% yield and selectivity within 5 min and TOF value was 77 times higher than those so far reported. They also observed that the yield was increased as the alkyl chain length of the IL’s cation was also increased from C₂ to C₈. Moreover, different epoxide substrates having phenyl substituted groups and alkyl side chain groups were examined for the synthesis of the corresponding carbonates in [emim][BF₄]–scCO₂ biphasic system at 14 MPa and 100 °C. Gao et al. [166] studied the transesterification between isoamyl acetate and ethanol in scCO₂, [bmim][BF₆] and [bmim][BF₄]–scCO₂ system using p-xylene sulfonic acid (p-TSA) as the catalyst. The results showed that the equilibrium conversion in [bmim][BF₄]–scCO₂ media was lower than those observed in scCO₂ or [bmim][BF₆]. An interesting application of IL–scCO₂ biphasic system in synthesis was electro-oxidation of benzyl alcohol to benzaldehyde in an electrochemical cell [167]. The reaction was carried out at 318.2 K and up to 10.3 MPa, and two ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), were used as the solvents and electrolytes. [bmim][BF₄] was a better medium for the electro-oxidation of benzyl alcohol. The Faradic efficiency (FE) and selectivity of benzaldehyde increased as the pressure increased up to 9.3 MPa, whereas the FE decreased as the pressure was increased further. The authors noted that the products could be easily recovered from the IL by using scCO₂ extraction after the electrolysis, and the IL could be reused. Yoon et al. [168] studied Heck coupling of iodobenzene with olefins in [bmim][PF₆] catalyzed by PdCl₂/Et₃N. They did not incorporate scCO₂ in the reaction, it was used after the reaction for product recovery.

IL–scCO₂ biphasic systems were also used for enzyme catalysis [173–179]. Lozano et al. [173–174] investigated the synthesis of butyl butyrate from vinyl butyrate and 1-butanol, and the kinetic resolution of rac-1-phenylethanol with vinyl propionate by transesterification. They used both free and immobilized C. antarctica lipase B (CALB) in IL ([emim][Tf₂N] and [bmim][Tf₂N]) as catalyst for continuous biphasic biocatalysis. CO₂ was used as transport medium for reactants and products. The synthetic activity of the enzyme in IL–CO₂ system was tested through operation/storage cycles. Operation period (4 h) was followed by a storage period (20 h) of the enzyme–IL system under dry conditions at room temperature. The continuous synthesis of butyl butyrate from vinyl butyrate and 1-butanol by transesterification was studied at 12.5 and 15 MPa at 40, 50 and 100 °C in [bmim][Tf₂N]–scCO₂ system [173]. The specific activity and the selectivity were enhanced as the temperature increased, the selectivity was high (>95%) in all cases giving higher than 50% conversions. The activity decay for the repetitive uses of the free enzyme–IL system was the highest at high temperature. The continuous synthesis of 1-octanol to benzaldehyde in an electrochemical cell (R)-1-phenylethyl propionate from the kinetic resolution of rac-1-phenylethanol with vinyl propionate catalyzed by free CALB dissolved in [emim][Tf₂N] and [bmim][Tf₂N] was also investigated at 15 MPa, 50 and 100 °C [173]. The results showed that the selectivity of the reaction, the activity and the half-life of the enzyme–IL system were lower for this reaction than those observed for butyl butyrate synthesis. However, high enantioselectivity (>99.9%) was exhibited by the enzyme. As the reaction temperature increased, the selectivity was increased but the specific activity decreased. In another publication of Lozano et al. [174], the continuous kinetic resolution of rac-1-phenylethanol in IL–CO₂ biphasic system was investigated at 120 and 150 °C and 10 MPa. Both free and immobilized CALB dispersed in [emim][Tf₂N] and [bmim][Tf₂N] were used as catalysts. [emim][Tf₂N] was a better IL in terms of obtaining higher initial synthetic activity and longer half-life time of the free enzyme–IL system. Immobilized enzyme–IL system had longer half-life time and higher synthetic activity compared to free enzyme–IL system. No activity losses during successive operation cycles were observed for immobilized enzyme at 120 °C and 10 MPa. Additionally, at the same operating conditions (120 °C, 10 MPa), in immobilized CALB–[emim][Tf₂N] system, high selectivity values (>98%) were always obtained for successive operation cycles, whereas in free CALB–[emim][Tf₂N] system, the selectivity increased from 36 to 98.5% as the number of operation cycles increased. Reetz et al. [175] studied the acylation of 1-octanol by vinyl acetate (batch and continuous mode) and kinetic resolution of 1-phenylethanol (batch mode), which were catalyzed by CALB in [bmim][BTA]–CO₂ system (BTA: bis(trifluoromethanesulfonamide)). The acylation of 1-octanol
by vinyl acetate in continuous mode was performed at 10.5 MPa and 45 °C. A total yield of 93.9% was obtained after 24 h. Reetz et al. [180] introduced a new method for enantiomer separation utilizing biocatalytic kinetic resolution and SCF extraction using an IL–scCO2 system. Application of this new method for separation of racemic secondary alcohols by CALB catalysis and CO2 extraction was represented. They converted several alcohols (2-octanol, 1-phenyl-ethanol, 3-methyl-2-butanol, 1-(2-phenylethyl) ethanol, and 1-(2-naphthyl) ethanol) enantioselectively to corresponding acetates and laureates by immobilized CALB suspended in [bmim][BTA], and separate (S)-alcohol from the product (R)-ester via CO2. Vinyl laureate was found to make the ester less soluble in CO2 than the alcohol, which allows for efficient separation, therefore it was used as the acylation agent. In that work, both batch and continuous modes of operation were studied. In batch mode, when vinyl laureate was used as the acylation agent, in the early fractions of isobaric extraction, the alcohol was extracted with high selectivity, whereas the lauryl ester was obtained with high purity in the later fractions. In order to speed up the extraction for the ester-rich fraction, they suggested increasing the CO2 density after most of the alcohol has been isolated. This procedure was successful for the separation of several alcohols and lauryl esters. Additionally, they include a separation chamber leading to a two-step extraction procedure. First, extraction was done at 60°C and 105 bar, then in the separation chamber the pressure was reduced to 80 bar and then the CO2 was vented through cryo-traps. By this procedure 66% of the theoretical amount of the alcohol under investigation was isolated with an enantiomeric purity >99.9% and less than 0.5% contamination with its corresponding lauryl ester. Then the pressure of reactor and the extraction chamber was increased to 200 bar and 89% of the theoretical amount of lauryl ester was isolated with an enantiomeric purity >99.9% and less than 1% contamination with alcohol. Kinetic resolution of rac-1-phenylethanol was used to demonstrate the continuous process. The separation after extraction was provided through two separation chambers with two steps of density reduction. After 112 h operation, 81% of the theoretical amount of the (S)-1-phenylethanol was isolated with an enantiomeric purity >97% and less than 0.1% contamination with its corresponding lauryl ester.

Lozano et al. [176] studied the synthesis of glycidyl esters from rac-glycidol catalyzed with free and immobilized forms of lipases from C. antarctica (CALA and CALB) and Mucor miehei (MML) in toluene, IL and IL–scCO2 (40, 50°C and 100, 150 bar). Four different ILs were used: [emim][NTf2], [bmim][PF6], [bmm][NTf2], and trioctylmethylammonium triflimide ([troma][Tf2N]). Using ILs instead of a classical organic solvent (toluene), and the increase in the alkyl chain length of the acylation agent had both positive effect on the enzyme activity and when these effects combined, the synthetic activity can be enhanced 95 times. CALA and MML favored the synthesis of R-glycidyl esters, whereas CALB favored the synthesis of S-glycidyl esters. CALB showed the highest activity among other enzymes. CO2 was used to transport the substrates and products. The synthetic activity of the free and immobilized lipases decreased in IL–scCO2 biphasic system, but the enantioselectivity remained unchanged with respect to the values obtained in only IL reaction media.

CALB catalyzed ester synthesis in IL–scCO2 biphasic systems with five different ILs ((3-hydroxypropyl)-trimethylammonium bis(trifluoromethylsulfonyl) imide [C3OHtma][NTf2]; (3-cyanopropyl)-trimethylammonium bis(trifluoromethylsulfonyl) imide [C3CNtma][NTf2]; butyl-trimethylammonium bis(trifluoromethylsulfonyl) imide, [C4tma][NTf2]; (5-cyanopentyl)-trimethylammonium bis(trifluoromethylsulfonyl) imide [C5CNtma][NTf2]; hexyl-trimethylammonium bis(trifluoromethylsulfonyl) imide, [C6CNtma][NTf2]) were studied by Lozano et al. [177]. The suitability of these ILs as enantiomeric reaction media was tested for the kinetic resolution of rac-phenylethanol by transesterification with vinyl propionate, and all of the tested ILs were found to be suitable media for enzyme catalysis. The synthetic activities and stabilities of the enzyme were determined in these five ILs. Then, the performance of CALB catalysis in IL–scCO2 biphasic system in continuous operation was tested for [C4tma][NTf2]–scCO2 and [C5CNtma][NTf2]–scCO2 systems at 50°C and 10 MPa for the synthesis of several short-chain alkyl esters (butyl acetate (BA), butyl propionate (BP), butyl butyrate (BB), hexyl propionate (HP), hexyl butyrate (HB), and octyl propionate (OP)), by transesterification from the respective vinyl alkyl esters with alkyl-1-ols. The results showed that the synthetic activity of CALB in ILs was higher than that in [C3CNtma][NTf2]–scCO2, even though the opposite result was obtained for activity values in pure IL. The authors concluded that rate-limiting parameters (synthetic activity and mass transfer phenomena between IL and scCO2 phases) were related with the solubility parameter of the IL’s alkyl chain and reagents.

Hernandez et al. [178] presented the synthesis of butyl propionate in scCO2 and IL–scCO2 using a recirculating enzymatic membrane reactor, in which α-alumina membranes were immobilized with CALB. The reactor was tested in only scCO2 at 50°C and 80 bar. In the second part of the study, the immobilized enzyme was coated with three different ILs, i.e. [bmm][PF6], 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [bdimim][PF6], [omim][PF6]. The selectivity was 95% when only scCO2 medium was utilized, and it increased to greater than 99.5% when IL–scCO2 biphasic system was used.

Lozano et al. [179] investigated the importance of the supporting material for the activity of immobilized CALB in IL–hexane and IL–scCO2 biphasic systems at controlled water activity. For this purpose they immobilized a commercial solution of free CALB onto twelve different silica supports, modified with specific side chains (e.g. alkyl, amino, carboxylic, nitrite, etc.) by adsorption. Both biphasic media was tested for the kinetic resolution of rac-phenylethanol by transesterification with vinyl propionate. CALB activity and stability was tested IL–hexane and IL–scCO2 biphasic systems with two different ILs: [btma][NTf2] and [toma][NTf2] (btma: butyl-trimethylammonium, toma: trioctylmethylammonium). The highest synthetic activity of immobilized enzyme was obtained for butyl-silica derivative, however for all supports, the selectivity for the reaction was higher than 94% except for the quaternary ammonium-Si support and the enantiomeric excess was greater.
The immobilized activity decreased 10 times in IL–hexane compared to that in only hexane, but half-life times were enhanced by up to six times. The synthetic activity of immobilized CALB increased by six times in IL–scCO$_2$ compared to that in hexane.

Recently, the potential of ILs to dissolve soil contaminants at ambient conditions and the ability of supercritical carbon dioxide (scCO$_2$) to recover these contaminants from IL extracts were mutually utilized to clean contaminated soils [181]. Naphthalene was used as the model component to represent a group of soil contaminants, and 1-$n$-butyl 3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) was used as the IL. The results demonstrated that soil contaminated with naphthalene was cleaned using [bmim][PF$_6$], and the amount of naphthalene remaining in the soil was below the allowable contamination limit. This study was the first in the literature which investigates the soil/model-contaminant/IL/scCO$_2$ system. On the basis of the findings a process flowsheet for the IL extraction of contaminated soils and continuous scCO$_2$ extraction of the contaminants from IL extracts was suggested and is given in Fig. 13.

8. Summary

This work aims to summarize and discuss the information present in the literature about ILs and IL–CO$_2$ systems. A great number of researchers investigated the high-pressure phase behavior of IL–CO$_2$ systems and concluded that CO$_2$ is highly soluble in most ILs, and ILs are not measurably soluble in scCO$_2$. The effects of pressure, temperature, nature of the anion and the alkyl chain length of the cation on the solubility of CO$_2$ reported by various studies are discussed and summarized here. Volatile and nonpolar scCO$_2$ has become a good partner of nonvolatile and polar IL and this new system with its unique properties have been utilized to extract organic compounds from ILs using scCO$_2$.

ILs are receiving more and more attention every day both in academic research and commercial applications and they seem as good replacements for volatile organic solvents. However, there is a discussion about the greenness of the ILs due to their incomplete physical, chemical and toxicological data. Although, there are some question marks related to the specific character-
istics of ILs, it seems that most of the researchers will continue to work with this new solvent, the developments of new applications utilizing ILs will increase rapidly and the number of publications will rise exponentially in the future. The present costs of the ILs are quite prohibitive in many probable commercial applications. However, there are hopes that in the near future, the cost/benefit figures of the ILs will bring economic viability to their more common use.

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