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## *Chapter 5*

# THE PHYSICAL AND CHEMICAL PROPERTIES OF IONIC LIQUIDS AND ITS APPLICATION IN EXTRACTION

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## ABBREVIATIONS

CE = capillary electrophoresis
CMC = critical micelle concentration
CMPO = octyl (phenyl)-N, N-diisobutylcarbamoylmethyl phosphine oxide
COSMO-RS= Conductor-like Screening Model for Real Solvents
CPE = cloud point extraction
DMCEAP = *N*, *N*-dimethyl(cyanoethyl)ammonium propionate
DMHEEAP = *N*, *N*-dimethyl-*N*-(2-hydroxyethoxyethyl) ammonium propionate
DNA = deoxyribonucleic acid
FAAS = flame atomic absorption spectrometry
FO-LADS = fiber optic-linear array detection spectrophotometry
FT-IR = fourier transform infrared spectroscopy
HPLC = high performance liquid chromatography
HRE = heat-reflux extraction
HSCCC = high-speed counter-current chromatography
ILAS-MA = ionic liquid aqueous solvent-based microwave-assisted hydrolysis
ILMAE = ionic liquid-based microwave-assisted extraction
ILs = Ionic liquids
IL-SIR-based = solvent (ionic liquid) impregnated resin-based

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| | | |
|---|---|---|
| ILUAE | = | ionic liquid-based ultrasonic-assisted extraction |
| LLE | = | liquid-liquid phase equilibria |
| MAE | = | microwave-assisted extraction |
| PEG | = | polyethylene glycol |
| QSPR | = | quantitative structure property relationship |
| RTILs | = | room temperature ionic liquids |
| Si-ILs | = | silica confined ionic liquids |
| SLM | = | supported liquid membrane |
| SPE | = | solid phase extraction |
| TODGA | = | N, N, N', N'- tetraoctyl diglycolamide |
| UAE | = | ultrasonic-assisted extraction |
| UV-Vis | = | ultraviolet-visible |
| VTF | = | Vogel-Tammann-Fulcher |

## ABSTRACT

Ionic liquids (ILs) as green solvents are attracting increasing interest from industry and academic in the whole world during past years. The researches on ILs are developing at an incredible rate. Their negligible vapor pressure, high thermal stability and relatively high viscosity make them different from the conventional organic solvents. This review focuses on the major physical and chemical properties of ILs related to the extraction application including polarity, pH value, melting point and solubility, etc. The review take some examples to illustrate the applications of ILs in various subjects of extraction, including extraction of biological molecular, active components from natural products, organic compounds from other resources except natural products and metal ions, etc. Current status of the application of ILs in the extraction and most significant achievements were reviewed. The comparison between traditional organic solvents and ILs in the application of extraction suggested that ILs would be a potential excellent solvent with wide application range in various extraction processes.

**Keywords**: ionic liquids; property; extraction.

## 1. INTRODUCTION

### 1.1. Overview

The ionic liquids (ILs) as a kind of green solvent have been widely used in synthesis and extraction. As well known, whether a solvent can be a potential extraction solvent is determined by some specific characteristics, such as density, viscosity, polarity. Certainly, ILs are not exceptional. The variety of ILs makes it nearly impossible to highlight its property. Their properties distribute in a wide range except ionic conductivity, but the ILs as extractant may have some common characteristics. So the properties related to extraction application of ILs need to be summarized. And ILs have one of most important characteristics is that ILs can be designed according to their application directions and concrete technical requests, so the summary in extraction property can also provide useful reference for target synthesis. The

ILs mainly used in extraction are imidazole-based. Other two such as pyridinium-based and N, N-dimethyl-N-R ammonium-based (see Figure1) are also used in extraction technology. The anion of IL used in extractions involves many types such as $BF_4^-$, $PF_6^-$, $CH_3SO_4^-$ and $(CF_3SO_2)_2N^-$.

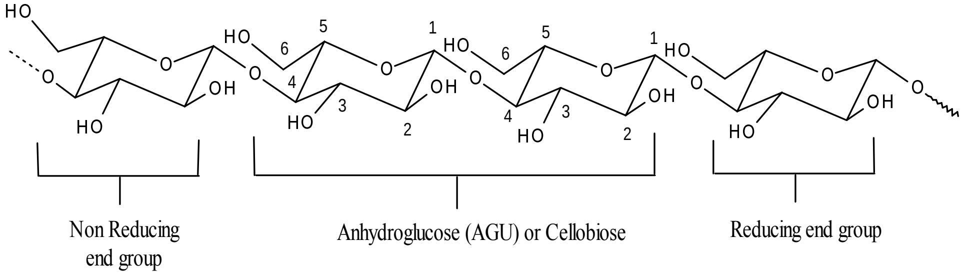

Figure 1. Three major types of cation of ionic liquids used in extraction.

The length of alkyl chain $C_nH_{2n}$ in imidazole-based ILs contains $C_2$, $C_4$, $C_6$ and $C_8$ that mostly used in extraction process, but the number of carbon atom sometimes may be more than ten when it is used in the extraction of hydrophobic compounds. At the beginning of this review, it is introduced about the popular ways of extraction using ILs.

## 1.2. Extraction Methods

### *1.2.1. Solvent of Direct Extraction*

The ILs as an extractant can be used in many extraction fields and have many benefits in extraction such as in the treatment of the radioactive wastes. The dispose of the radioactive wastes was a challenge for chemists and environmental workers. In the past, N, N, N’, N’-tetraoctyl diglycolamide (TODGA) was considered to have many advantages for extraction of minor actinides. However, its major drawback is associated with a large volume of n-dodecane used as a process diluent, which tends to form a third phase with nitric acid [1] and generates a large amount of the secondary waste. In addition, potential health hazard and flammability risk are also associated with it [2]. Application of ILs called green solvents could avoid the above risks due to ILs with low vapor pressure and low toxicity. Besides as extractant in radioactive wastes dispose, the ILs also were widely reported as extractants in extraction of metal ions.

### *1.2.2. Liquid-Liquid Extraction*

Liquid-liquid extraction, a conventional extraction method easily used in industrial scale, was recently used with ionic liquids. There have been lots of reports about aromatic organic compounds extracted by ionic liquids [3, 4]. With their non-volatile property, the ILs can be simply recovered to avoid high investment and energy cost which is hard to avoid by using conventional solvents. The ILs have been widely used in the extraction of benzene, toluene, ethyl benxene and xylenes, etc. [3]. Shiflett *et al.* [5] recently extracted the tetrafluoroethylene and carbon dioxide using 1-butyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide.

As a green solvent, ILs may be broad prospects in liquid-liquid extraction process. The common liquid-liquid extractions with ionic liquids were shown in Table 1 [3, 6-18].

**Table 1. The common liquid-liquid extraction systems**

| Extraction object | Extraction phase | Ionic liquid | Reference |
|---|---|---|---|
| Aromatic | Aliphatic | [mebupy][$BF_4$]/[Epy][$EtSO_4$] | [3, 6-8] |
| Phenols | Aqueous solution | [$C_n$mim][$PF_6$]/[Cnmim][$BF_4$] | [9] |
| Thiophene | n-Alkanes | [$C_8$mim][$BF_4$] | [10] |
| L-amino acid | Ethylacetate/aqueous solution | Amino acid ionic liquids/hydrophobic ionic liquids | [11,12] |
| Butanol | Dilute aqueous solution | [hmim][$Tf_2N$] | [13] |
| Protein | Aqueous solution | [Btmsim][$PF_6$] | [14,15] |
| Uranium | Aqueous solution | Hydrophobic ionic liquid | [16] |
| Ferulic Acid/Caffeic acid | Aqueous solution | [$C_6$mim][$PF_6$] | [17] |
| Linalool | Citrus essential oil | [$C_2$mim][Meesu] | [18] |

### *1.2.3. Two Phase Extraction*

As early as 2003, Rogers and his co-workers reported aqueous two-phase extraction systems based on ILs and water-structuring salts for the first time [19]. Two-phase extraction system was different from normal liquid-liquid extraction. In the former extraction the IL phase directly extracts objects to form a solution. In the latter extraction the IL solution extracts object and then some IL phase or other reagents used to extract objects in second time from the IL solution for enriching the objects. The two phase extraction was early used by the polymer combining with water [20]. But there is another problem that is the polymer can hard to recover from the water. Hence, the ILs became the objects to form two phase used in extraction. The ILs can form two phases with many materials such as polymer, water, phosphate and amino acids [19, 21, 22]. Jiang and co-workers [21] extracted penicillin to imidazole-terminal PEG-rich phase then used ionic liquid to extract imidazole-terminal PEG, last they recovered 1-PEG to water for recovering polymer. In the same year, Pei *et al.* extracted proteins by ionic liquid-based aqueous two-phase extraction. The ILs can form two phases with various materials, the IL application in two phase extractions will be extended.

### *1.2.4. Combined with Other Solid Phase*

Solid phase extraction (SPE), which was thought to be as an acceptable alternative to liquid-liquid extraction, has been widely used in the separation, purification, and solvent exchange of solutes from a solution [23, 24]. Major SPE mediums related with ILs extraction technology include anion-exchangeable silica confined IL, ILs on nano-silica sorbents and IL impregnated resin-based extraction. In those extraction processes with above mediums, ILs display their functions through different binding ways to various supporters. Silica confined ILs (Si-ILs) were also already used in chromatographic separation with their excellent physical and chemical properties [23]. Bi *et al.* [23] successfully extracted lactic acid from fermentation broth by anion-exchangeable Si-ILs. Hydrophobic ILs on nano-silica sorbents used in extraction metal from water sample were recently investigated by Mahmoud [25]. In his research, two newly modified nano-silica sorbents were synthesized. The results showed that the newly synthesized amino functionalized nano-silica hydrophobic IL sorbents were experienced with high surface coverage and area as well as high efficiency in lead (II) extraction providing high metal capacity values compared with other methods [25]. IL impregnated resin-based (IL-SIR-based) extraction was found to be able to avoid many drawbacks of conventional SPE method and liquid-liquid extraction [26]. The method of preparation for the IL-SIR was directly making resin immerse to a solution containing IL. The IL-SIR-based extraction offers a number of important benefits, such as less consumption of ILs, retaining properties of ILs, higher mass transfer rate, high recovery rate of target compounds and easy recovery of the adsorbent [26].

### *1.2.5. Combining with Membrane*

Membrane separation is a conventional separation method and widely used in extraction technology. The supported liquid membranes (SLM) technique is a combination of three simultaneously occurring processes: molecule extraction from the feed phase to the SLM, diffusion through SLM and re-extraction to the received phase [27]. The ILs inject new vitality to membrane separation technology. The supported membrane includes ILs supported liquid membrane and hollow fiber supported IL membrane. The technology of ILs supported liquid membrane coats the liquid membrane with IL and needs low investment and operating cost, low energy consumption, low liquid membrane requirement and simple to operate [28]. The SLM was thought to have wide application areas involving extraction of organics from water, gas, amino acids, toxic metal ions from their aqueous solution and separation of isomeric organic compounds [29]. The unique properties of ILs were thought to have potential application in industrial separation for membrane technology. Malik *et al*. [29] reviewed the IL supported liquid membrane techniques and Lozano *et al*. [27] summarized the recent advances in supported IL membrane technology. Hollow fiber based liquid phase microextraction was introduced in last century and it has been widely used in separation process. In this process, one most important factor is the selection of organic solvent which determines the extraction efficiency. Toluene and 1-octanol are usually selected as conventional solvents. ILs have been proven as a good solvent in this process [30] and display excellent extractability for various organic compounds and metal ions. Hollow fiber supported IL membrane microextraction was used in determination of sulfonamide and chlorophenols and so on. Furthermore, ILs can make the subsequent analysis simpler.

### *1.2.6. Ionic Liquid Supported Cloud Point Extraction*

Cloud point extraction (CPE) is a novel separation and pre-concentration technology. When the nonionic surfactant solution is at a concentration at least 3~20 times of its critical micelle concentration (CMC) and at a temperature higher than its cloud point, phase separation occurs [31]. Conventional surfactant such as polyethoxylated nonionic surfactants and non-ionic surfactant Triton X-114 were usually used as the separation agent in CPE procedure [2, 3, 32] and this technology has been used in various samples and objects [2, 3, 32, 33]. Recently ILs were found to be used in cloud-point extraction [34] because that ILs were gaining recognition as unique solvents for environmental applications and its usage in CPE technology has far-reaching significance. BMIM $PF_6$ has been examined for CPE by Pavagadhi *et al*. [34] in their paper. In their study, the IL was used to treat the water by removing the most commonly reported toxin microcystin-leucine-arginine (MCLR). For environment and health requirements, the environmentally friendly pre-concentration methods are needed without compromising the sensitivity and specificity of the conventional methods. Therefore, ILs as a green solvent was a good choice to meet those requirements and the results showed excellent application in CPE.

#### *1.2.7. IL Dispersive Liquid-Liquid Microextraction*

The microextraction was mainly used in trace determination of samples before detection by various chromatography methods. Microextraction techniques are very useful and popular for the pre-concentration and separation of organic and inorganic contaminants in environmental samples at trace levels since the last ten years. In addition, the liquid-liquid microextraction was also used in treatment of natural products. It has many advantages like simple procedure, high extraction efficiency and low consumption of toxic organic solvents [35]. The ILs dispersive liquid-liquid microextraction has been used in extraction and enrichment of target analytes for various analytical methods such as high performance liquid chromatography (HPLC), capillary electrophoresis (CE), flame atomic absorption spectrometry(FAAS) and fiber optic-linear array detection spectrophotometry (FO-LADS). With the appearance of more and more new ILs, the IL dispersive liquid-liquid microextraction will be used in wider areas.

## 2. RELATED PHYSICAL AND CHEMICAL PROPERTIES

As everyone knows, the practicability of the application of ILs, especially in extraction was considerably determined by physical and chemical properties of ionic liquids such as density, viscosity, polarity, pH value and so on. However, the designability of properties is one of most important characteristics and advantages of ILs. Previous researches also showed that the design of properties-suitable ILs for specific requirement was totally feasible. For example, according to the regular relationship between the polarity and structure of ILs, the ILs with certain polarity can be designed. Obviously, a clear understanding about ILs' physical and chemical properties is crucial for its application in extraction.

### 2.1. Density

The density of ILs will determine the separation form of ILs in extraction process. The density is the most often measured and reported physical property of ILs for its importance in related applications. ILs are generally denser than organic solvents, with typical density values ranging from 0.9 to 1.7 g $cm^{-3}$. Many of the reported density values are at a single temperature, usually at 20 or 25 $^{o}$C. The density of ILs versus pressure and temperature has also been modeled. Considerable amounts of data on the density of ILs are available in the literatures and reports of temperature parameters (always linear) are most valuable.

In general, the density of matter is not only related with the temperature and pressure, but also with the relative molecular mass, the interaction between molecules and molecular structure. The density of ILs is greatly affected by the anions and cations. Anion is usually more significant on the density. Via comparing the imidazole cations with different substituents, the density is linear to the alkyl chain length of substituents. Larger organic cations usually have lower density. The density was affected by the molecular weight of the anions, which was related to the molecular frame volume and free volume of the room temperature ionic liquids (RTILs). In particular, the density significantly varies according to the conjunction (single bond, double bond, chainlike, or cyclic) and conformation (planar or non-planar) of the species.

Reported densities of ILs vary between 0.9 and 1.7 g $cm^{-3}$ and are little sensitive to temperature [36]. For example, Kato and Gmehling [37] presented data for 1-butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide in the range of (298.15~323.15)K, it showed variation of only 0.9% in the density.

Fisher Company [38] provided a density formula for dialkylimidazolium IL at different temperatures:

$$\rho = a + b\,(T- 60)$$

where ρ is the density in $kg{\cdot}m^{-3}$; T is the temperature in K; *a*, *b* were estimated by published experimental data.

**Table 2. The coefficients a and b of some ionic liquids**

| Ionic liquid | a/(g/cm$^3$) | b/10$^{-4}$(g/cm$^3$K) | Ionic liquid | a/(g/cm$^3$) | b/10$^{-4}$(g/cm$^3$K) |
|---|---|---|---|---|---|
| [BMIM]$BF_4$ | 1.1811 | 7.6229 | [OMIM]$PF_6$ | 1.1960 | 9.2302 |
| [HMIM]$BF_4$ | 1.1242 | 7.2090 | [HMIM]Cl | 1.0593 | 6.3026 |
| [BMIM]$PF_6$ | 1.3381 | 8.5275 | [OMIM]Cl | 0.9999 | 3.6033 |
| [HMIM]$PF_6$ | 1.2596 | 10.2938 | | | |

Fredlakc [39] gave a deep research on the density of ILs at different temperatures. When the temperature rises, the volume of all the ILs has different degrees of expansion, which leads to the decrease of the density.

Since it is difficult to study properties of all compounds at different conditions, it is necessary to find a method to estimate properties of compounds. It seems very important to predict the property before an IL is synthesized for its functionality. The quantitative structure property relationship (QSPR) is often used to predict density of ILs. The record indicates that QSPR models could give a reasonable prediction of unknown or unavailable compounds of the same class. Trohalaki *et al* [40] reported a QSPR method to estimate the density.

There have been some other methods in the estimation of the IL density. Gardas *et al.* [41] successfully extended Ye and Shreeve's group contribution method [42] for a wide range of temperature and pressure.

In this method, the average relative deviation of estimated densities for imidazolium-based and phosphonium-based ILs can be 0.45% and 1.49%, respectively. And some other methods were reported to estimate the temperature-dependent densities of ILs. In Ref [43], a different estimation method of the heat capacity and temperature-dependent density of ILs was presented.

## 2.2. Viscosity

Viscosity is another important factor of ILs in affecting its application in extraction, which is generated by the motion and molecular interaction between the molecular. Viscosity of ILs usually is reported as the dynamic viscosity and also called the viscosity coefficient. Most ILs are viscous liquids and inherently much more viscous than molecular solvents. Viscosities of ILs vary over a range of <10 to >1000 cP at room temperature. Viscosity affects diffusion of solutes and practical issues, such as stirring and pumping. So, high viscosity is a major disadvantage since it negatively will affect mass transfer and power requirements for mixing in heterogeneous liquid-liquid systems.

Viscosity-temperature dependence of ILs is more complicated than that of most molecular solvents, because most ILs do not follow ordinary Arrhenius behavior. Most temperature studies fit the viscosity values to the Vogel-Tammann-Fulcher (VTF) equation, which adds an additional adjustable parameter (glass transition temperature) to the exponentially term.

The increase of length of alkyl chains of the cation does not necessarily result in a monotonous increase in the viscosity. Huddleston *et al*. [44] found that for the series of $[C_nMIM][PF_6]$ with n in alky chain of [CnMIM] equal to 4, 6 and 8, the viscosity at 25 $^oC$ increased monotonously from (450 to 682) mPas. Bonhote *et al*. [45] found that for alkyl chain lengths from 1 to 4 on 1-alkyl-3-methylimidazolium $Tf_2N-$, the viscosity first decreased and then increased again. At present it is believed that there is insufficient data on fluids of well defined purity to make any definitive conclusions. As noted, the high viscosity of ILs does not appear when ILs are used in chemical processing. These high viscosities facilitate suspending larger drops at the tip of a capillary or needle for liquid-phase microextraction but otherwise contribute to poor penetration of porous solid materials and restrict mass transfer at solvent interfaces [46]. MacFarlane *et al*. [47] prepared a new family of RTILs based on the dicyanamide anion $N(CN)_2^-$. Among them, $[Emim][N(CN)_2]$ has a melting point at $-21^{\circ}C$ and its viscosity at $25^{\circ}C$ is 21mPa s. Liquids with viscosities of this magnitude would not present processing problems. This is a limitation for some methods such as countercurrent chromatography. The viscosity of ILs can be lowered into a useful range for some applications by increasing the temperature or by dilution with a miscible solvent [48].

## 2.3. Melting Point

The melting points of IL solvents define the lower end of the liquidus range. Compared with molecular solvents, the low vapor pressure and very wide liquids range are probably the two meaningful properties that make the ILs very attractive as solvents. Many or most ILs are prone to supercooling, which makes melting points difficult to measure. Many ILs can form glasses and ILs's glass transition temperatures are usually reported instead of melting points. The glass transitions tend to be very low ($<-50\ ^{\circ}C$) and viscosity very high at such cold temperatures, so the solvents are not really useful for most reaction chemistry at sub-zero temperatures (except for situations where glassy media are desirable).

For a substance to be considered as a RTIL, its melting point should be below 100 $^{\circ}C$. The main factors that influence the melting point are the charge distribution on the ions, H-bonding ability, the symmetry of the ions and the van der Waals interactions. The melting points of many ILs are very uncertain because they undergo considerable supercooling. The supercooling of ILs causes their freezing point to be notoriously unreliable and irreproducible.

References [49-52] made systematic studies of the influence of the alkyl chain on the melting points of RTILs. In general, the melting point, if observed, decreases from the methyl substitution to the butyl to hexyl compound and then increases. However the studies come to different conclusions because in some studies only glass temperature transition was observed for many of the C4 to C8 compounds. Some of the glass transition temperatures were reported as melting points.

Katritzky *et al.* [53] used QSPR to predict the melting points for 126 structural diverse pyridinium bromides. They found that the statistically most important parameters were the coordination ability of cations determined by molecular shape and symmetry, electrostatic intermolecular interactions and the number of conformational and rotational degrees of freedom in the solid and liquid phases.

## 2.4. Polarity

Solvents polarity is another important factor which remarkably influences ILs application in extraction, more knowledge about the polarity of ILs can give a positive impetus to the further application of ILs.

Due to the multitudinous peculiar features of ILs compared with the ordinary molecular solvents, we can not lump together the polarities of ILs and molecular solvents. The solvent polarity can not be simply defined, but we often consider polarity as an indicator of the combined strength of specific solute–solvent interactions and nonspecific solute-solvent interactions. The special solute-solvent interactions, according to the previous study on the polarity in ILs, can be understood as the same mechanism of that in ordinary molecular solvents to a certain extent. The nonspecific solute-solvent interactions, such as electrostatic interaction, appeared to be more complex and unpredictable.

To investigate the polarity of ionic liquids, the methods researchers commonly use include solvatochromic dyes and partition coefficient methods and so on [54]. Among them, the most common method is using solvatochromic dyes, which are a variety of compounds, such as Nile Red and betaine-30, for which the absorption or emission band maxima varies with the polarity of the solvents in which they are dissolved. Through the comparison between the absorption spectra of solvatochromic dye in series of conventional solvents and ionic liquids, the polarity of the ILs can be determined.

On the study of the polarity of ILs a lot of significant work has been done. For example, Carmichael and Seddon [55] used Nile Red to investigate the polarity of room-temperature ILs based on the 1-alkyl-3-methylimidazolium cation. Their research provided information about their relative polarity and trends within the series, and the polarities in these ILs appeared in the same region with 2-aminoethanol and the lower alcohols, such as methanol, ethanol and 1-butanol, etc.

Kobrak’s work [56] showed that there is definite relationship between the polarity and the molar volume in ionic liquids. Although the results were not quantitatively accurate, the study made the prediction of polarity of ionic liquids possible, and furthermore, researches can design polarity-specific ionic liquids according their research requirements.

Znamenskiy and co-workers' research [57] showed that controlling the polarity of ILs through the specific interactions is feasible. They neglected the nonspecific interactions and only considered the specific solute-solvent interactions, and then the variety of the polarity of ILs can be seen as a function of ionic structure.

Anyway, because of the hydrophobic of alkyl chains, as same as ordinary organic compounds, ILs with long chain branching are generally hydrophobic, while those hydrophilic ILs always has no chain branching or their chain branching are very short. Correspondingly, the longer the chain branching of ILs is, the stronger polarity ILs have.

## 2.5. Acid and Basicity of Ionic Liquids

### *2.5.1. Acid Ionic Liquid*

Acid ILs can be divided into Lewis acid and Brønsted acid ILs. The *lewis* acids were obtained by mixing the metal halide and Halogenated phosphorus salt by different mole fraction, for example, the ILs [BMIM]Cl/ZnCl$_2$, [BMIM]Cl/CuCl, [BMIM]Cl/FeCl$_3$ and [BMIM]Cl/AlCl$_3$.

Brønsted acid ILs were obtained by introducing acid groups. Common Brønsted acids are shown in Figure 2. The acidity of Brønsted acids is determined by their acid group. According to reference [38], when chain length of carboxylic acid chain increased, the acidity of imidazole based ILs decreased such as [C5emim]$^+$<[C4emim]$^+$<[C3emim]$^+$. When the cations of ILs were the same, the acidity of ILs changed by the following order: Cl$^-$>BF$_4^-$ >CF$_3$SO$_3^-$.

The acidity of anions in ILs may influence the extraction efficiency. Imidazole based ILs with different anions were studied to show the influences of acidity of anion in extraction. The acidity order of anions was as follows: PF$_6$>Tf$_2$N> BF$_4$.

The methods to detect the acid ILs were reported by some researchers. Wang *et al*. [58] overviewed these methods mainly containing Hammett indicator method, Potentiometric titration method and FT-IR probe molecular determination method. The Hammett indicator method has been widely used to approximate the acidity of a pure IL. Cox *et al.* [59] used 3-nitroaniline as an indicator to measure the Hammett acidity. The IR spectrum by using probe molecular with special absorption peaks can be used to detect the acidity of different solid and liquid Lewis and Brønsted acidic substances. Pyridine is the most commonly used probe molecular and will change the position of IR absorption peaks of ILs when it is added into the latter. Cao *et al.* [60] used FT-IR method by employing acetonitrile as molecular probe to characterize the [bupy] BF$_4$-MCl$_3$ (M = Al, Fe) ILs. They found the acidity strength of [bupy] BF$_4$-AlCl$_3$ was stronger than [bupy] BF$_4$-FeCl$_3$. Potentionmetric titration method is mainly used to study the ion exchangers for ILs [61]. Zhao *et al.* used this method detected the acidity of a series of ILs [38].

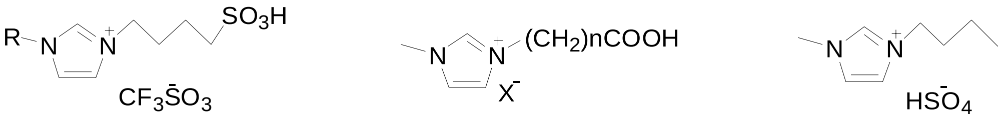

Figure 2. Several common Brønsted acidic ionic liquids.

### *2.5.2. Basic Ionic Liquid*

Similar to acid ILs, basic ILs also can be divided into Lewis basic and Brønsted basic ILs. Mehnert found the neutral ILs such as [BMIM] $BF_4$ can become basic ILs mixed with strong base such as NaOH or KOH [38]. Li *et al.* [62] summarized the basic ILs in his review. Besides the ILs from the strong base, some new basic ILs were reported by researchers [63, 64]. The Brønsted basic ILs was prepared by introducing basic groups. Common basic ILs are showed as Figure 3. The basity of Brønsted acids were decided by their basic group, and their basity levels were decided by the basity levels of the basic groups.

Figure 3. Several basic ionic liquids.

The reports about basicity detection of ILs were rare. Some researchers [65] used Hammett indicator method to identify the basicity of ILs. But these methods only gave a qualitative result by comparing with traditional base such as NaOH [wenxian]. The basity order of ILs was as follows: [Bmim][OH] > [Bmim][IM] and [NH2Emim][IM]> [NH2Emim]Br. The characterization of basic ILs need advance investigation.

### *2.5.3. The Acid and Basic Ionic Liquids in Extraction*

The acidity-activity relationship has been studied by many researchers. There were seldom studies about the relationship between acidity or basicity and extraction efficient. But the influence of pH value in extraction procedure was found to be a very important factor in actual applications, which could influence the partition coefficients of the extraction object and determine the presence species of object. When the ILs are used in extracting acids, the extraction rate would increase if the basity of anions is stronger. For example, in the extraction of 3-indole butyric acid, the percent extraction was higher by using $C_n$mim$BF_4$ than that using $C_n$mim$PF_6$ [66]. When the ILs were used in extraction, the pH value of extraction systems was almost lower than pka value of the used ILs to maintain the combination ability of with the anion of ILs.

## 2.6. Solubility

When in choice of ILs for extraction application, the solvation ability is always a key factor, because the solvation ability of ILs actually directly determines if it can be employed as an extraction solvent. Consequently knowledge about the solvation characteristics of ILs is essential to the use of ILs in separation.

For the ordinary dipolar liquids such as acetonitrile, forming a space to offer to solute molecule needs a cost of some units of kcal/mol to remove some solvent molecules, while in ILs it needs a cost of some hundreds of kcal/mol. This is because every ion in ILs is surrounded by a discrete number of counter ions. Only when the solute-solvent interaction can overcome the needed energy, the solvation can occur.

According to Amstrong and co-workers' research, ILs can dissolve solutes through a variety of forces, such as dipole-dipole interaction, hydrogen bond, π-π interaction of imidazole ring and so on [67]. Rogers and co-workers' showed that neutral substances have better solubility in ILs, while the ionized substances tend to be dissolved in water rather than in ILs [68].

However, the solvation mechanism in ILs is not clear yet; some studies think mechanism of ILs is similar to that of polar organic solvents. Because of many unique properties of ILs, we can not consider the dissolving behavior in ILs as same as that in ordinary organic solvents.

Despite the lack of adequate understanding of the solvation mechanism, considerable achievements on the study about the solvation in ILs have been made. For example, previous research showed that ILs could dissolve a wide and varied range of organic and inorganic compounds in reasonable mole ratios. Most of ILs could form homogeneous system with polar organic solvents such as ethanol and acetone, while biphasic system could form if ILs are mixed with water or low polar organic solvents, such as acetic ether, ether and methylbenzene, etc. [69].

In recent years, the study on the separation in two-phase systems with a pure IL phase has been getting more and more attention. For example, it has been proved that [Bmim][$BF_4$] can be used to extract erythromycine-A by Cull *et al* [70]. There is also a few researches to find that when [$C_6$mim] [$PF_6$] was used to extract the amino acids the partition coefficients were pretty high [71].

After all, because most ILs have strong polarity, they can dissolve many organic or inorganic compounds and polymeric materials. And they can also dissolve hydride, carbide, nitride, oxides and sulfides [72]. Obviously, satisfactory solvation ability makes ILs very attractive as extraction medium.

## 2.7. Binary Property

A clear understanding of liquid-liquid phase equilibria (LLE) between ILs and organic solvents is of great importance to the related application of the ILs, especially in the industrial application point of view, because it determines whether the ILs can be easily reused to a certain degree. Simultaneously, LLE also plays a key role in the extraction process. According to previous researches, in a binary system comprised of IL and alcohol, factors including the alcohol chain length, the cation chain length and subsistent groups of ILs all influence the phase behavior [73]. For instance, the solubility of ILs in alcohol normally usually decreases with the growth of the number of the C atoms the alcohol has, and the miscibility between ILs and water shows apparently decreasing with the increasing of cation chain length.

The study of Andreia Forte *et al* [74] proved that both the structure of ILs and alcohols affect the phase behavior. They investigated twenty binary systems containing ILs, and the results showed that the systems comprised of hydrophilic dicyanamide ILs and polyhydroxy alcohols were completely miscible, while the systems containing Bis(trifluoromethylsulfonyl)amide ILs show low solubility with butane-1,2-diol and its structural isomers.

Considering the huge number of ILs, however, it's impossible to actually measure all the systems. In view of this, Klamt *et al* [75] proposed a model called Conductor-like Screening Model for Real Solvents to predict the LLE of binary systems. This model can almost be suitable for all possible ILs and hydrocarbons mixtures. Although it is unable to provide the accurate data of LLE, the systems can be designed to satisfy our need according the qualitative trend of the phase behavior it predict.

About the prediction of the properties of binary systems, Navia and co-workers [76] also did some meaningful works. Their research showed that there were not too much excess properties in binary systems comprised of ILs and other solvents, which meant the properties of binary mixtures could be accurately predicted based on the pure compound properties.

## 3. EXTRACTION APPLICATIONS

### 3.1. Extraction of Metal Ions

More and more metallic substances in the environment caused by human's industrialization have been a serious threat to ecological environment and, in extreme case, human healthy. For lots of heavy metals ions, such as cadmium, once they enter the human body, it is hard to be excreted from the body and the concentration will be increasing through the accumulation, and it reaches a certain concentration which even leads to the death.

Besides the harmfulness of the metals to environment, sometime the recovery of valuable metals, such as silver, is also worthy to do from an economic point of view.

Obviously, a simple and effective separation of metals is of significant importance. In past, methods like precipitation, solvent extraction and ion exchange method were taken to remove or recover metals [77], and among them solvent extraction shows many advantages and has been widely used. However, the conventional solvent extraction makes secondary pollution caused by the volatility of the organic solvents. As mentioned above, the use of ILs can treat this situation for their nonvolatile. ILs as an extractant has been fairly widespread. But the extraction mechanism is still controversial yet, and the most convincing point is cation-exchange mechanism [78], that is metal cation transferring to the ILs phase through the metal cation exchanging with the cation of IL.

About the extraction mechanism lots of work have been carried out. For instance, Kazunori Nakashima and co-workers used octyl (phenyl)-N, N–diisobutyl carbamoyl methyl phosphine oxide (CMPO) to extract rare earth metals from aqueous solutions, and the results showed that the extraction efficiency and selectivity was higher than that when using the n-dodecane as extractant. Moreover, they also found that the extraction efficiency of the IL system decreased with the increasing of $[Bmim]^+$ concentration, while the dodecane system showed no relationship with the $[Bmim]^+$ concentration at all. This phenomenon confirmed the cation-exchange mechanism to a certain extent.

De los Rios and co-workers [79] investigated the extraction of $Zn^{2+}$, $Cd^{2+}$, and $Fe^{3+}$ from aqueous hydrochloride solutions using six ILs $[MTOA^+][Cl^-]$, $[omim^+][BF4^-]$, $[omim^+][PF6^-]$, $[bmim^+][PF_6^-]$, $[bmim^+][NTf_2^-]$ and $[omim^+][NTf_2$-], as exhibited in Figure 4. The results showed that $[MTOA^+][Cl^-]$ can almost completely extract the all three metal ions, and so do the $[omim^+][BF_4^-]$ for the $Zn^{2+}$ and $Cd^{2+}$. Furthermore, because there is no extraction of $Fe^{3+}$ using $[omim^+][BF_4^-]$, $[omim^+][BF_4^-]$ can selectively extract $Zn^{2+}$ or $Cd^{2+}$ from $Fe^{3+}$ . Similarly, $[bmim^+][PF_6^-]$, $[bmim^+][NTf_2^-]$ and $[omim^+][NTf_2^-]$ can also make selective separation of $Cd^{2+}$ or $Fe^{3+}$ from $Zn^{2+}$ possible. All of these results demonstrated that the application of ILs in extraction of metals is very promising.

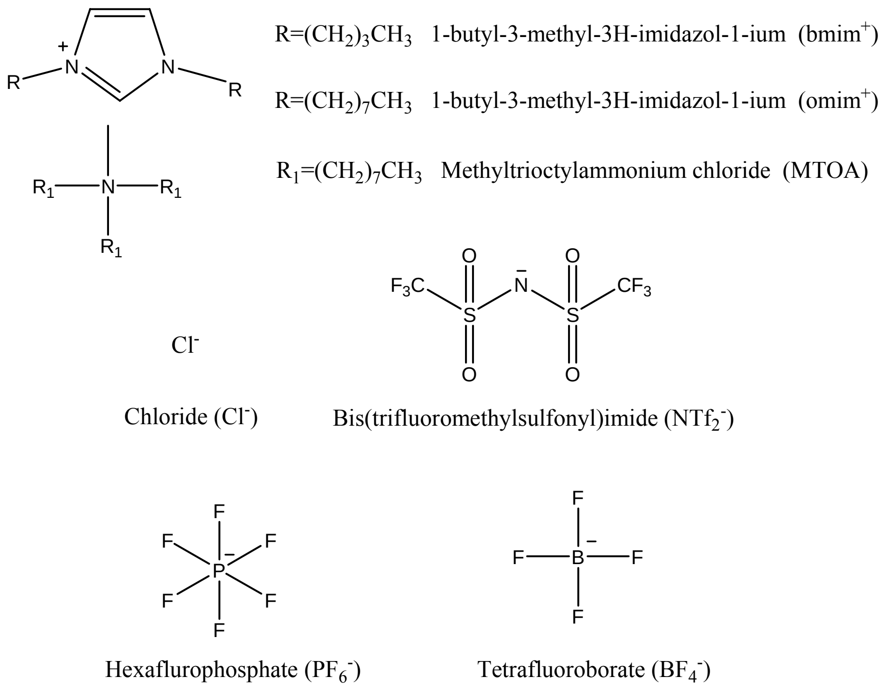

Figure 4. Ions involved in the assayed ionic liquids [76].

Papaiconomou and co-workers [80] also achieved the selective extraction of copper, mercury, silver and palladium ions from water using hydrophobic ILs as extractant. They compared ten ILs and the results in their study showed that all the studied ILs formed two liquid phases when mixed with water, and except that mercury ion could be extracted well by the ILs containing octylpyridinium cations, other metal ions were not significantly extracted by all these ILs.

Moreover, it was reported that the following ions $Cd^{2+}$, $Hg^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Fe^{3+}$ can be extracted with $[BMIM][BF_4]$ and $[C_6MIM][PF_6]$ [81]. $Cs^+$ and $Sr^{2+}$ can be extracted using ILs in the presence of crown ether [82]. And selective extraction of $Cu^{2+}$ and $Ag^+$ using ILs were proved to be feasible by Wei, etc [83]. Luo and co-workers showed $K^+$ and $Na^+$ can also be extracted by ILs [84].

## 3.2. IL Extraction of Organic Molecules

The specific advantages and limitations of ILs in these studies were discussed with a view to defining the future uses of IL extraction. ILs are good solvents for a wide range of compounds in which they behave as polar solvents. Their physical properties of note that distinguish them from conventional organic solvents are a negligible vapor pressure, high thermal stability, and relatively high viscosity. In this section, the extraction of phenolic compounds will be as an example to show the application of ILs in separation on organic compounds. As illustrated in Table 3 [85-89], phase partitions of many phenolic compounds are summarized in the IL-water biphasic systems.

**Table 3. Examples of IL extractions of organic/bio/biofuel molecules**

| | Substances | IL | Extractant | Reference |
|---|---|---|---|---|
| Phenolic compounds | Phthalic acid, aniline, 4-hydroxybenzoic acid, benzoic acid, p-toluic acid, benzene, chlorobenzene, Phenol, tyrosol, p-hydroxybenzoic acid | [BMIM][PF6] | none | [85] |
| Amino acids | Chlorophenols, Tryptophan, glycine, alanine, leucine, lysine, arginine | [BMIM][PF6] | DC18C6 | [86] |
| Carbohydrates | Xylose, fructose, glucose, sucrose | [CnMIM][X] (n = 4, 6, 8, 10; X = Cl$^-$, PF6$^-$, BF4$^-$) | none | [87] |
| Organic acids | Lactic acid, acetic acid, glycolic acid, propionic acid, pyruvic acid, utyric acid | [CnMIM][PF6] (n = 4, 6, 8) | TBP (in some cases) | [88] |

Another process was developed to separate C4-8 diolefin hydrocarbons (such as butadiene) from at least one diolefin and at least one C1-18 paraffin using ILs (such as [BMIM][BF$_4$] [89]). A continuous extraction process using IL to separate C6-9-aromatic hydrocarbons has also been developed, from benzene-rich petroleum streams [90].

The academicians are often overtly optimistic while laboratory analysts have a long tradition of conservativism. What is clear is that the proof of concept and feasibility studies completed in academia has not obtained sufficient weight so far to establish the use of room temperature ILs in routine laboratory practice. The green shoots of development seem closer to fruition in process chemistry driven mainly by the unique physical properties of ILs that allow them to be used as economic and environmentally friendly eplacements for conventional organic solvents at a time when such actions are seen as being politically correct.

More recently, various ILs were found to be green solvents for cellulose dissolution [91] and suitable reaction media for cellulose functionalization [92]. The high concentration of chloride and its activity in ILs are considered to play an important role in cellulose dissolution, which is highly effective in breaking the extensive hydrogen- bonding network present in cellulose. A similar observation on the degradation of cellulose in ILs was reported by Heinze *et al.*[93]. They found that the dissolution of spruce sulfite pulp and cotton linters in [C$_4$mim]Cl led to slight degradation, and DP of cellulose after regeneration decreased from 593 to 544 for spruce sulfite pulp and from 1198 to 812 for cotton linters, respectively.

### 3.3. Extraction of Bioactive Components from Natural Products

Currently, ILs have been successfully used in extraction of bioactive components from natural products (as shown in Table 4) [34, 94-109] in these years. The advantages of using microwave-assisted extraction (MAE) in the extraction of organic compounds directly from solid matrix have been demonstrated in recent years, and it is considered that ILs can efficiently absorb microwave energy as solvents and co-solvents [110]. Application of ILs as solvent in MAE of bioactive components from natural products was reported by many research groups. A series of 1-alkyl-3-methylimidazolium ILs with different alkyl chain and anion composition were evaluated with their extraction efficiency. The obtained results indicated that the anions and cations of ILs had influences on the extraction efficiency. Du and coworkers [97, 98] were developed IL-based microwave-assisted extraction (ILMAE) methods for extraction *trans*-resveratrol from *Rhizma Polygoni Cuspidati* and lycorine, lycoramine and galanthamine from *Lycoris*, and the results demonstrated the potentiality of ILs as alternative solvents in MAE. Compared with HRE technique, ILMAE could obtain higher extraction yield by using less solvents at short extraction time. And in their latest article, the application of acid ILs aqueous solvent-based microwave-assisted hydrolysis (ILAS-MAH) technique was developed for the extraction of myricetin and quercetin from *Myrica rubra* (*M. rubra*) leaves [95]. Different from the conventional procedures, the proposed ILAS-MAH was a rapid and effective method with a higher yield without volatile solvent consumption. Chi and co-workers [104] investigated a microwave-assisted extraction method to extract senkyunolide I, senkyunolide H and *Z*-ligustilide from *Ligusticum chuanxiong* Hort, and two protic ILs, *N*, *N*-dimethyl-*N*-(2-hydroxyethoxyethyl) ammonium propionate (DMHEEAP) and *N*, *N*-dimethyl (cyanoethyl) ammonium propionate (DMCEAP), were employed as extractants. After extraction, IL was extracted by n-hexane to recover target compounds. The concentration of senkyunolide I and senkyunolide H hardly decreased, but the concentration of *Z*-ligustilide decreased by 39.7%, these results might be caused by the solubility of the protic ILs towards the organic solvent. The extraction mechanism of the investigated microwave assisted ILs extraction was the same as traditional organic solvent extraction.

IL surfactants are a class of ILs, which can form micelles in the aqueous solution. Wu and coworkers [96] developed a novel extracting system based on the use of IL surfactants in ultrasonic-assisted extraction (UAE) of tanshinones from *Salvia miltiorrhiza* bunge, and they found that the carbon chain length exerts a significant impact on the extraction performance, and no traditional organic solvents was used in the extraction, which made this method environmentally friendly and more attractive than the conventional organic solvent-based extraction. UAE as one of the promising extraction techniques can offer high reproducibility in shorter time, simplified manipulation, reduced solvent consumption and temperature and energy input [111]. Cao group investigated an IL-based ultrasonic-assisted extraction (ILUAE) method for extraction piperine from white pepper powder [102]. Compared with the conventional heat-reflux extraction (HRE) and regular UAE, the optimized approach gained the highest extraction efficiency (from 1.950% to 3.577%) within the shortest extraction time (from 2 h to 30 min). Sun and coworkers developed an IL based ultrasonic-assisted extraction method for the extraction of the three isoflavones, tectoridin, iristectorin B and iristectorin A from *Iris tectorum* Maxim, which were separated and purified by high-speed counter-current chromatography (HSCCC) [98]. Under the optimized ILUAE conditions, the highest extraction yields of tectoridin, iristectorin B and iristectorin A were 37.45, 2.88 and 5.28 mg/g, respectively. These results indicated that the combination of application of ILUAE and HSCCC was a very powerful technique for the extraction and preparative separation of tectoridin, iristectorin B and iristectorin A from *I. tectorum* dried roots.

**Table 4. Extraction of effective components of natural products**

| Source | Ionic liquid | Target compounds | Extraction method |
|---|---|---|---|
| *Myrica rubra leaves*[95] | [BMIM][$HSO_4$] | Myricetin and quercetin | MAE |
| *Salvia miltiorrhiza bunge*[96] | [$C_{16}$MIM][Br] (IL surfactant) | tanshinoneI, tanshinone IIA, and cryptotanshinone | UAE |
| *Lycoris radiata*[97] | [BMIM][Cl] | lycorine, lycoramine and galanthamine | MAE |
| *Rhizma Polygoni Cuspidati*[98] | [BMIM][Br] | trans-resveratrol | MAE |
| *Iris tectorum Maxim*[34] | [OMIM][Br] | Tectoridin, iristectorin B and iristectorin A | UAE |
| *Lonicera japonica Thunb*[99] | [BMIM][$BF_4$] | Chlorogenic acid | UAE |
| *the fruit of Schisandra chinensis Baill* [100] | [$C_{12}$MIM][Br] | Biphenyl cyclooctene lignans | UAE |
| *Nelumbo nucifera Gaertn* .[101] | [BMIM][$BF_4$] and [HMIM][$BF_4$] | Liensinine, isoliensinine and neferine | MAE |
| *White pepper (Piper nigrum L.*[102] | [BMIM][$BF_4$] | Piperine | UAE |
| *Cynanchum paniculatum*[103] | [BMIM][Cl] | Paeonol | LLE |
| *Ligusticum chuanxiong Hort.*[104] | N,N-dimethyl-N-(2-hydroxyethoxyethyl) ammonium propionate (DMHEEAP) and N,N-dimethyl(cyanoethyl)ammonium propionate (DMCEAP) | lactones | MAE |
| *Saururus chinensis (Lour.) Bail. (S. chinensis) and Flos Sophorae*[105] | [BMIM][Tso] | Rutin | MAE |
| *Stephaniae tetrandrae*[106] | [BMIM][$BF_4$] | Fangchinoline and tetrandrine | UAE |
| *lotus leaf*[107] | [HMIM][Br] | N-nornuciferine,O-nornuciferine, and nuciferin | MAE |
| *Psidium Guajava Linn. leaves and Smilax china tubers*[108] | [BMIM][Br] | Gallic acid, Ellagic acid, Quercetin, tran-Resveratrol | MAE |
| *Corydalis saxicola Bunting*[109] | [HMIM][Br] | Dehydrocavidine | MAE |

## 3.4. Extraction of Biological Substances

Biological substances were different from other materials due to their unique application and potential prospects in the areas about food, health, environment and energy. The extraction of biological substances here refer in particular to the application of ILs in the extraction of the substance about protein, amino acids, enzyme, biofuel and biofeedstock, which has many restrictions due to their unique properties and their special uses. The traditional toxic organic solvent sometimes can not be used in the extraction of some substances when the productions are used in the areas of food or health. Furthermore, the extractants in extractions of biological substances have many limitations in their some physical properties. Taking the protein for example, the protein is sensitive to pH value, temperature, metal salt and some organic solvents which all may cause protein inactivation or degeneration. ILs have been successfully used in the extraction of protein for a few years. This section will take some examples to illustrate the application of ILs in the relative extraction process.

### *3.4.1. Proteins*

The first example that showed is that the extraction of proteins by using ILs. The proteins about life technology are not suited to toxic organic solvent. The green ionic liquids became the alternative extractant to be employed in processing proteins. The extraction of proteins by ILs has several characteristics as follows:

First, early extraction of proteins by using ILs needed a concomitant extractant or two-phase extraction for the low solubility of proteins in ILs. Proteins of bovine serum albumin, trypsin, cytochrome c and γ-globulins were extracted efficiently by aqueous two-phase extraction systems based on imidazolium ILs [112]. With the development of extraction research, Cheng *et al*. [113] reported that the heme-protein was extracted into IL without using any concomitant reagent or extractant in 2008 for the first time. In their study, the hemoglobin was been extracted from human whole blood with $\text{BtmsimPF}_6$ and the quantitative extraction had arrived a certain level. The directly extraction by using ILs will extend to more proteins with the target synthesis of novel ILs.

Second, the extraction environment was various and this suggested that ILs can be used in many complex conditions. The extraction objects include yeast, blood and so on [113, 114]. Yeast is thought to be an important model in the study of biological science. It is not only used in the research of genetics and basic biological process of cells, but also the industrial production of various proteins. But the harder cell wall make it is more difficult to get proteins from it. Recently, ILs were used in cell disruption stage for extraction of proteins. The investigation of Ge *et al.* [114] indicated that the IL [DMAPA]FA was a promising reagent for protein extraction in yeast cells.

Third, the IL can be used in the extraction of different kinds of proteins such as hemoglobin, bovine serum albumin, trypsin, cytochrome c, and γ-globulins.

Finally, the extraction of proteins by ILs was influenced by many factors and the activity of proteins could be maintained after extraction. The protein extraction was influenced by temperature, pH value and IL concentration. One most important thing in protein extraction was that the conformation and activity of proteins can not be changed in the whole extraction procedure. The research of Pei *et al.* [112] suggested that both the conformation and activity were maintained in the IL-rich phase of the aqueous two-phase system, hence it proved the safety of ILs indirectly. Besides directly extracting proteins, the ILs have also been indirectly used in these procedures.

### *3.4.2. Animo Acids*

Amino acid is an important biological molecular and the basic unit of proteins. The amino acids have been widely used in food and health. As an important nutrients and drugs, the recovery process of amino acids is necessary. Some amino acids (L-tryptophan, L-phenylalanine, L-tyrosine, L-leucine and D-valine) were recovered from aqueous media by ILs [115]. The ILs were used in extracting neutral, acid and basic amino acids. Absalan *et al.* employed imidazolium-based ILs as extractant to study the partitioning behaviors of typical neutral (Alanine), acid (Glutamic acid) and basic (Lysine) amino acids [116]. Besides above applications, the amino acids were good model to be used in investigate the basic partition data, the influence factors, the extraction and the molecular level interactions behind the extraction. In recent years, the amino acid ILs were studied in the extraction of chiral separation of amino acids. For example, Tome *et al.* [12] took the amino acid L-tryptophan as model biomolecule to make a detailed study of the chiral extraction and the factors in extraction procedure above.

### *3.4.3. DNA*

Deoxyribonucleic acid (DNA), the famous molecular in biology is a macromolecule polymer. DNA is a very important bimolecular and fundamental ingredient of many organisms, which can be used in several research areas. It can help study the life activity, heredity and be used in authenticate. But all these must be done in what premise of separation and purification. The degradation of DNA in extraction procedure must be avoided. The isolation of double-stranded DNA by 1-butyl-3-methylimidazolium hexafluorophosphate was showed here quoted from the reference [117]. The results showed that the ILs can successfully avoid the degradation of DNA. Besides avoiding the degradation, they successfully extracted DNA when the trace amounts of DNA was at the levels of <5 ng microL-1. The two advantages above ensure the safety and effectiveness in the extraction of DNA by using ILs, which was better than traditional organic solvents.

### *3.4.4. Biofuels and Biofeedstocks and Other Biomolecules*

The range of biofuel and biofeedstocks is very wide. Methanol, ethanol, 1-propanol, 1-butanol, and various other organic compounds can be produced biologically, and thus can be considered as biofuel candidates, as biofeedstocks for production of other chemicals, and as biobased solvents for various applications [118]. Conventional production of biofuels and biofeedstocks were costly for the high cost of post processing energy. Because of the advantageous characteristics of ILs,ILs as a potential extractant can be used in liquid-liquid extraction of biofuel and biofeedstocks. For example, Simoni *et al.* [118] focused on the extraction of 1-butanol from a dilute aqueous solution by ILs and successfully used 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide to extract it from water. Besides the biomolecular mentioned above, extraction of other biomolecular by ILs were also studied [119, 120]. Tzeng *et al.* [120] used a dye-modified IL to extract the lysozyme by employing liquid-liquid extraction. ILs modified with other materials have also been summarized in

Tzeng's paper. Young and co-workers [119] extracted bio-oils from biomass by the IL-polar covalent molecule co-solvent systems. The ILs can handle different samples contained many kinds of biomass. Huang *et al.* [121] extracted biogenic amines by IL-based ultrasonic-assisted liquid-liquid microextraction method from beer samples.

The ILs have many advantages in the extraction of biological molecules as follows: 1. ILs were thought as low or even no toxic solvent and they were suited in dealing with products such as food and drugs related with human health; 2. It was thought the activity and conformation of proteins can not be changed in extraction procedure; 3. ILs can handle different samples in various kinds of environments; 4. The aftertreatment of ILextraction technology was thought to be lower energy consumption and lower cost because of its unique characteristics. With the development of ILs, it will be alternative to the organic solvent and may be better than conventional extractants.

## CONCLUSIONS

Conventional extraction with organic solvents or water has limitation or flaw for their inherent drawbacks. As a kind of green solvent, ILs are used in extraction procedures by more and more researchers due to its unique physical properties and application potential. Its obvious advantages make it can not only be used in different kinds of targets and tasks, but also can save the energy and reduce the cost in its recovery and post processing. The physical and chemical properties of ILs related with extraction were reviewed in this article. ILs are devisable solvents and their synthesis is not difficult. The summary of its properties about extraction can give suggestions to the target synthesis of functional ILs which can be used in separation and purification fields. The extraction of four typical kinds of molecules was reviewed and new advances in these applications were also summarized. With the emergence of more and more ILs, they will be applied in wider range in the near future.

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