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Ionic Liquid as Novel Solvent for Extraction and Separation in Analytical Chemistry

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1. Introduction

Direct analysis of samples, regardless their origin, is desirable although for the majority of cases unfeasible on account of the complexity of the sample matrix, inadequate concentration of the target analytes, or even incompatibility with the detector. In these cases, a sample pretreatment step is required for interference removal and analytes separation/preconcentration. Despite valuable advances developed in separation science, the traditional solvent extraction is widely used for samples preparation. Main drawback of the solvent extraction is the requirement of large amounts of high-purity solvents that are expensive and toxic and result in the production of hazardous waste. Therefore, the search for new solvent is a key trend in solvent extraction evolution. In this sense, ionic liquid, which is ionic media resulting from the combination of organic cations and various anions, has attracted much attention taking into account their special features like: low-vapor pressure, high viscosity, dual natural polarity, good thermal stability and a wide range of miscibility with water and other organic solvents, hence many environmental and safety problems associated with organic solvents are avoided. As a result of their unique chemical and physical properties, the ionic liquid has aroused increasing interest for their promising role as alternative medium for classical solvent extraction [1-7] and organic synthesis [8-10].

Recently, ionic liquids were rapidly developed as environment-friendly acceptor phase for various microextraction to sample preparation in analytical chemistry such as liquid phase microextraction, single drop liquid phase microextraction, solid phase microextraction, dispersive liquid phase microextraction and cold induced aggregation microextraction. The microextraction with ionic liquid often exhibited better extraction efficiency and enrichment factor than that with conventional solvent extractions. Among the microextractions, dispersive liquid phase microextraction is very rapid and effective. Since the ionic liquid is dispersed completely into aqueous phase and the analytes will more easily migrate into the ionic liquid phase because of the much large contact area, the procedure for dispersive liquid phase microextraction may be complete within several minutes. In recent years, the ionic liquid extraction coupled with different analytical technology has widely been applied to determination of ultra trace analytes in water or other samples such as high performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC-MS) for organic compounds, and flame atomic absorption spectrometry (AAS) and graphite furnace atomic absorption spectrometry (ETAAS) for metal ions. In general, the extractions with...
ionic liquid have increasingly become the most important samples preparation technologies in analytical chemistry.

2. Application of ionic liquids as medium for classical solvent extraction

2.1 Metal ion extraction and its application

For metal ion extraction, one needs to find the right combination of ionic liquid and ligand to obtain similar behavior as in organic solvents or one needs to use the differences from organic solvents for achieving more advantageous separations. Although the metal ion extraction in the ionic liquid/aqueous two phase system often indicated high efficiency and selectivity that excelled most of organic solvents, the metal ion partitioning always rely on the species of the ionic liquid, metal ion and ligand seriously. For examples, Bartsch group reported on the influence of structural variations in room temperature ionic liquid on the selectivity and efficiency of competitive alkali metal salt extraction by crown ethers [11]. They showed that extraction efficiency generally diminished as the length of the 1alkyl group on the ionic liquid was increased. It was demonstrated that metal ion affinity for the hydrophobic phase necessitates the presence of an extractant [12]. Professor Rogers has investigated Cyax-923 as an ligand for actinide ions in liquid/liquid separation using the hydrophobic ionic liquid [C$_{10}$mim][Tf$_2$N] as the extracting phase, a mixture of tri-alkyl-phosphine oxides of varying mixture of tri-alkyl-phosphine oxides of varying chain lengths (hexyl- and octyl-) and has been used for actinide extraction into molecular solvents. Distribution ratio measurements for Pu$^{4+}$ and Am$^{3+}$ showed little acid dependency for Pu$^{4+}$, but strong acid dependency studies seem to support 1:1 metal:ligand binding for Pu$^{4+}$, but significantly the notion that ionic liquids can provide different coordination environments [13]. In such application, imidazolium cations were also derived to include the task specific functionalities, such as metal ligating groups that when used as part of the solvent or doped in the less expensive ionic liquids could dramatically enhance the extraction of targeted metal ions [14]. Moreover, the effect of pH on the extraction efficiencies showed a big difference due to its differences in solvent behavior of ionic liquid and conventional organic solvents. After metal ion was extracted to ionic liquid, a strong solution such as nitric acid was applied to stripping metal ion from the ionic liquid. We have investigated the conditions of stripping metal ions from ionic liquid too, the experiments indicated metal ion is easy to be stripped from ionic liquid phase and enter aqueous phase if the neutral complex was formed in a base medium. Otherwise, metal ion stripping required a relatively strong base solution. However, the stripping process is slow very much at room temperature. In order to overcome the problem, a new stripping procedure was developed for stripping metal ion from ionic liquid, in which the equal volume of acetone and the ionic liquid containing metal ion complex mixed before a strong solution was added, whole process can complete within several minutes. At the same, above stripping method may be used to renew of the ionic liquids.

Recently, we attempt that metal ion extraction in the ionic liquid/aqueous two phase system combined with spectrometry technology including AAS and spectrophotometry to determine ultra trace amounts of metal elements in environmental samples. It was found that the extraction procedure can decrease the detect limit and improve the selectivity of analytical method remarkably. For atomic absorption spectrometry, the metal ion extraction must be back-extracted into aqueous solution, then was introduced into atomic absorption spectrometer for determination. For example, a new room temperature ionic liquid
[C₄tmsim][PF₆] was developed as a novel medium for liquid/liquid extraction of inorganic mercury with CDAA, the extraction and back-extraction efficiencies were 99.9 and 100.1% for 5.0 µg.L⁻¹ standard mercury in 1000 mL of water solution, respectively, the detection limit is 0.01 µg.L⁻¹ mercury in real water sample, proposed method has been used to the determination of trace inorganic mercury in natural water with satisfactory results [8]. If the ionic liquid phase containing metal complex is transparent, it can be directly used to spectrophotometric determination. So that, metal ion extraction in the ionic liquid/aqueous two phase system in which some excellent chromogenic reagent was selected as ligand to form metal complex is very selective, this may overcome the drawback in sensitivity of conventional spectrophotometric methods. For example, we reported a highly sensitive and selective extraction spectrophotometric method for determination of trace germanium in natural water with a new chromogenic reagent methybenzeneazosalicylfluorone abbreviated as MBASF, in which ionic liquid [C₄mim][PF₆] was used as novel medium for liquid/liquid extraction of germanium (IV). In the presence of TritonX-100, MBASF reacted with germanium (IV) to form a red complex rapidly, the complex was then extracted into the [C₄mim][PF₆] phase (shown in Fig.1), absorbance of the complex in ionic liquid at 496 nm was recorded and used to determine trace Ge⁴⁺. The apparent molar absorptivity of the complex and the detection limit for the real sample were found to be 3.12×10⁶ L.mol⁻¹.cm⁻¹ and 0.2 ng.mL⁻¹ respectively. The absorbance of the complex at 496 nm increases linearly with the concentration up to 4mg of Ge⁴⁺ in 250 mL of aqueous solution. The interference study show the determination of germanium is free from the interference of almost all positive and negative ions found in the natural water samples. The determination of Ge⁴⁺ in natural water was carried out by the present method and ETAAS. The results were

![Fig. 1. Absorption spectrum of the reagent against water (1), the complex in the aqueous phase (2), and in the [C₄mim][PF₆] (3), germanium (IV): 4.0mg in 250 mL of aqueous solution, [C₄mim][PF₆]](www.intechopen.com)
satisfactorily comparable so that the applicability of the proposed method was confirmed using the real samples [40]. Metal ion extraction in ionic liquid/aqueous two phase system and their application were listed in Table 1.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Ionic liquid</th>
<th>Ligand</th>
<th>Detection technology / detection limit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni²⁺, Fe³⁺, Cu²⁺, Mn²⁺, Cd²⁺</td>
<td>[C₄mim][PF₆], trioctylmethylammonium salicylate</td>
<td>1,10-phenanthroline</td>
<td>ETAAS/1.0 ng mL⁻¹</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], ionic liquid functionalized 2-mercaptobenzothiazole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], PAN</td>
<td>ammonium pyrrolidine dithiocarbamate and diethylidithiocarbamate</td>
<td>FI-FAAS/12.5 μg L⁻¹</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], AAS</td>
<td></td>
<td></td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone</td>
<td>AAS/0.70 μg L⁻¹</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 2-mercaptobenzothiazole</td>
<td>AAS/4.6 ng L⁻¹</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], DCH-18-C-6</td>
<td></td>
<td></td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], tri-n-butyl phosphate</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 2-aminothiophenol</td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 2-thenoyltrifluoroacetone</td>
<td></td>
<td></td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 2-thenoyltrifluoroacetone</td>
<td></td>
<td></td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], tri-n-butyl phosphate</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 2-pyridinealdoxime</td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 3,5-ditertbutylsalicylfluorone</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], dithizone</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 3,5-dibromo-4-chlorosalicylfluorone</td>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>[C₄mim][PF₆], 2,4-dinitrophenol</td>
<td></td>
<td></td>
<td>29</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Metal</th>
<th>Ionic Liquid</th>
<th>Method</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb²⁺</td>
<td>[C₄mim][PF₆]</td>
<td>dithizone</td>
<td>ETAAS/1.0 ng.L⁻¹</td>
</tr>
<tr>
<td>Sc³⁺</td>
<td>[C₄mim][PF₆]</td>
<td>Cyanex-925</td>
<td>35 ng.L⁻¹</td>
</tr>
<tr>
<td>M²⁺</td>
<td>[C₄mim][PF₆]</td>
<td>benzoyl trifluoroacetone, 2-naphthoyl trifluoroacetone and trifluoroacetylacetone</td>
<td>36 ng.L⁻¹</td>
</tr>
<tr>
<td>Pd²⁺</td>
<td>tri-n-octylmethylammonium chloride and tri-n-octylmethylammonium nitrate</td>
<td>Aliquat-336</td>
<td>37 ng.L⁻¹</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>[C₄mim][PF₆]</td>
<td>1-methylimidazole</td>
<td>38 ng.L⁻¹</td>
</tr>
<tr>
<td>La³⁺</td>
<td>[C₄mim][PF₆]</td>
<td>N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine</td>
<td>39 ng.L⁻¹</td>
</tr>
<tr>
<td>Ge⁴⁺</td>
<td>[C₄mim][PF₆]</td>
<td>methybenzeneazosalicylfluorone</td>
<td>Spectrophotometry/0.2 ng.mL⁻¹</td>
</tr>
<tr>
<td>UO₂²⁺, Am³⁺, Nd⁵⁺, Eu³⁺</td>
<td>[C₄mim][Tf₂N]</td>
<td>dialkylphosphoric or dialkylphosphinic acids</td>
<td>41 ng.L⁻¹</td>
</tr>
<tr>
<td>UO₂²⁺, Cu²⁺</td>
<td>[C₄mim][PF₆], [C₄mim][Tf₂N]</td>
<td>tri-n-butylphosphate, beta-diketonate</td>
<td>42 ng.L⁻¹, 43 ng.L⁻¹</td>
</tr>
</tbody>
</table>

Table 1. Reviews in extraction of metal ions with ionic liquid as medium

### 2. Organic compound/gas extraction and separation

Ionic liquids have been widely applied to organic compound/gas extraction and separation too. Basing on the ionic liquid various unique solvent characteristics and extraction performance, room temperature ionic liquids may be used as liquid membrane materials to separation organic compound and gas. For example, [C₄mim][PF₆] as membrane solution can be utilized for hydrocarbon separation by using a supported liquid membrane. Although the permeation rates through the membrane based on the ionic liquids were less than those of water, the selectivity of aromatic hydrocarbons was greatly improved [45]. Ionic liquid as special solution combined with classical separation technologies such as liquid/solid phase microextraction was used to beforehand separation and enrichment of the sample for high performance liquid chromatography, this may improve the separation effect of analytical technology remarkably. Ionic liquid as electrolyte can enhance electric capability to capillary zone electrophoresis. For example, professor Qi reported the ionic liquid used as running electrolyte in capillary zone electrophoresis with cyclodextrin (β-CD) as modifier for the separation of anthraquinones extract of Chinese herb Paedicalyx attopevensis Pierre ex Pitard [46]. Ionic liquid as ion pair reagent was applied to reversed-phase high performance liquid chromatography. Moreover, utilization of supercritical carbon dioxide (scCO₂) in concert with various popular ionic liquids is shown...
to have modified and enhanced the overall extraction capabilities and applications of these neoteric solvents$^{[47-50]}$. Brennecke group have investigated the recovery of organic products from ionic liquids using scCO$_2$. The results indicated the recovery rates of various aromatic and aliphatic solutes from [C$_4$mim][PF$_6$] in the presence of environmentally benign scCO$_2$ are presented. In a subsequent study, interesting outcomes showing utility of scCO$_2$ as a separation switch for ionic liquid/organic mixtures were published by the same group$^{[47, 48]}$. In general, we conjecture ionic liquid will rapidly be applied to many new fields of the extraction and separation with understanding on the extraction performance of room temperature ionic liquid.

3. Application of ionic liquids in microextractions

3.1 Liquid phase microextraction

Ionic liquid has been widely applied to various liquid phase microextractions for sample preparation. Commonly, volume of the ionic liquid for liquid phase microextraction is often lower than 25 µL in order to obtain high enrichment factor. To fine mix the ionic liquid with aqueous phase, a relatively long extraction time and strong stir process are strongly required. However, so small volume of the ionic liquid is difficult to be precisely collected from aqueous phase due to its dissolution in water and adhere to wall of the vial (Table 2). To overcome the problems, some new types of liquid phase microextraction have been reported in literatures. For examples, single drop microextraction (SDME) (Table 3) and dispersive liquid microextraction (DLME) (Table 4).

<table>
<thead>
<tr>
<th>Analyte: Steroidal antiinflammatory drugs</th>
<th>Ionic liquid [C$_4$mim][PF$_6$]</th>
<th>Sample: Human urine</th>
<th>Remark: Enrichment factors varied between 10.69 for naproxen and 13.93 for fenbufen. HPLC system was employed for analysis. A dynamic liquid-phase microextraction using an ionic liquid as acceptor phase is reported.</th>
<th>Ref. 51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyte: Aromatic and aliphatic hydrocarbons</td>
<td>Ionic liquid [C$_4$mim][PF$_6$]</td>
<td>Sample: Water</td>
<td>Remark: GC-MS was coupled with determination of analyte; for the first time hollow fiber-protected ionic liquid supported three-phase (liquid-liquid-liquid) microextraction; enrichment factor and extraction time are 210 and 40 min.</td>
<td>Ref. 52</td>
</tr>
<tr>
<td>Analyte: 4-Nonylphenol, 4-tert-octylphenol</td>
<td>Ionic liquid [C$_4$mim][PF$_6$]</td>
<td>Sample: Water</td>
<td>Remark: HPLC was employed for analysis; enrichment factors are between 19.5 and 33.8, and extraction time was about 30 min.</td>
<td>Ref. 53</td>
</tr>
<tr>
<td>Analyte: Chlorpromazine, promethazine, levomepromazine, prochlorperazine</td>
<td>Ionic liquid [C$_4$mim][PF$_6$]</td>
<td>Sample: Human urine</td>
<td>Remark: HPLC was employed for analysis.</td>
<td>Ref. 54</td>
</tr>
</tbody>
</table>
trifluoperazine, fluphenazine and thioridazine

Phorate, parathion and poxim

Benzene, toluene, ethylbenzene, and xylene, polycyclic aromatic hydrocarbons, phthalates, phenols, aromatic amines, herbicides, organotin, and organomecury

Chlorpromazine, promethazine, levomepromazine, prochlorperazine, trifluoperazine, fluphenazine and thioridazine

Cobalt

Triazines

Palladium

Cadmium

Table 2. Reviews for common liquid phase microextraction using ionic liquid as acceptor phase

SDME includes direct-immersion liquid phase microextraction and headspace liquid phase microextraction. Because during headspace liquid microextraction the ionic liquid has no loss because it lack effective vapor pressure even at high temperature, headspace liquid phase microextraction often provide a higher enrichment factor for most of analytes than direct-immersion liquid phase microextraction. A typical experimental set-up of headspace liquid phase microextraction is illustrated in Fig.2 [59]. Before each extraction, the microsyringe was rinsed with methanol to avoid analyte carry-over and air bubble

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Fig. 2. Schematic diagram of SDME formation. For the extraction an aliquot of the sample solution was placed in a vial immersed in the recirculating cell. After the uptake of the 10-25 µL of the ionic liquid, the microsyringe needle was inserted through the septum and then tightly fitted with a long polytetrafluoroethylene tube, and the syringe to begin with the extraction process, the syringe plunger was depressed completely to expose an ionic liquid drop and the magnetic stirrer was turned. After extracting, the magnetic stirrer was switched off, and then the microdrop was retracted back into the microsyringe and injected directly into detector for analysis. SDME is based on the equilibrium of the three phases: the condensed aqueous phase, the headspace phase and the microdrop phase. Mass transfer in the headspace is assumed to be a faster process since diffusion coefficients in the gas phase are typically 10^4 times greater than corresponding diffusion coefficients in the condensed phase. Thus, both slow mass transfers in the aqueous phase and diffusion of analyte into the microdrop are limiting steps in the overall extraction process was clamped so that the tip of the needle was located in a constant position in the headspace of the vial. The penetration theory indicates the aqueous phase mass transfer coefficient of solute increases with increasing stirring rate, and heating improves the mass transfers in the aqueous phase and induces convection in the headspace. Therefore, consequently the equilibrium between the aqueous and vapor phase can be attained more rapidly. Moreover, an addition of salt (such as NaCl and Na₂SO₄ etc) to the sample can decrease the solubility of analytes in the aqueous phase and enhance their partitioning into the organic phase, the extraction is often enhanced with increasing salt concentration and polarity of compound. Thus, a salt concentration of about 30 % was used in most SDME.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ionic liquid</th>
<th>Sample</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzenes</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>HPLC was coupled with analysis; extraction time is 37min; an obvious salting-out effect was observed.</td>
<td>57</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>[C₄mim][PF₆]</td>
<td>Shiitake mushroom</td>
<td>2,4-Dinitrophenylhydrazine was used as derivative agent; HPLC was coupled</td>
<td>58</td>
</tr>
<tr>
<td>Component</td>
<td>Ionic Liquid</td>
<td>Solvent</td>
<td>Analysis Method</td>
<td>Results</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>-----------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Dichlorodiphenyltrichlorethane and its metabolites</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>HPLC was coupled with analysis; extraction time is 30min</td>
<td>obvious salting-out effect was observed; effect of salting-out is obvious.</td>
</tr>
<tr>
<td>Phenols</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>GC was used for detection of phenols; enrichment factors were in the range from 17.2-161.7.</td>
<td></td>
</tr>
<tr>
<td>Chloroform, bromodichloromethane, dibromochloromethane and bromoform</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>HPLC was employed for analysis; extraction time was about 30min; an obvious salting-out effect was observed well.</td>
<td></td>
</tr>
<tr>
<td>Chlorinated anilines</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>HPLC was employed for analysis; extraction temperature and salting-out effect on the extraction performance.</td>
<td></td>
</tr>
<tr>
<td>Benzopine-3</td>
<td>[C₄mim][PF₆]</td>
<td>Urine</td>
<td>GC-MS was employed for the analysis; a new removable interface that enables the introduction of the extracted analytes into the GC system, while preventing the ionic liquid from entering the column, has been developed.</td>
<td></td>
</tr>
<tr>
<td>Benzene, toluene, ethylbenzene and xylene isomers</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>GC-MS was employed for the analysis; extraction temperature and salting-out effect on the extraction performance.</td>
<td></td>
</tr>
<tr>
<td>Cobalt, mercury and lead</td>
<td>[C₄mim][PF₆]</td>
<td>Biological and environmental samples</td>
<td>Electrothermal vaporization inductively coupled plasma mass spectrometry was employed for determination; after 10 min of extraction, the enrichment factors were 350 (cobalt), 50 (mercury) and 60 (lead); 1-(2- pyridylazo)-2-naphthol as both extractant and chemical modifier.</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzenes</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>A 20 min of extraction time was required; a microwave was used for assist extraction.</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>ETAAS was employed for analysis; 1-(2-thiazolylazo)-2-naphthol was used for chelator of manganese; the drop of the ionic liquid was directly injected into the graphite furnace.</td>
<td></td>
</tr>
<tr>
<td>1-Naphthylamine, N,N-dimethylaniline and diphenylamine</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>Enrichment factors are in the range from 13.7 to 116.3.</td>
<td></td>
</tr>
<tr>
<td>4-Dichlorophenol, naphthol, 2-nitrophenol and 4-chlorophenol</td>
<td>[C₄mim][PF₆]</td>
<td>Water</td>
<td>The effect of complex matrices natural water samples could be resolved with addition of sodium ethylene diamine tetracetate into the samples.</td>
<td></td>
</tr>
</tbody>
</table>

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| 4-Nonylphenol, 4-tert-octylphenol | [C₆mim][PF₆] | Water | HPLC was employed for analysis; the proposed procedure has a detection limit and enrichment factor of 0.3 μg.L⁻¹ and 163 for 4-nonylphenol, and 0.7 μg.L⁻¹ and 130 for 4-tert-octylphenol, respectively. |
| chlorobenzenes | [C₆mim][PF₆] | water | Limits of detection ranging between 1 and 4 ng.L⁻¹. |
| mercury species | [C₆mim][PF₆] | water | Limits of detection were between 1.0 and 22.8 μg.L⁻¹ for the four species of mercury. |
| lead | [C₆mim][PF₆] | certified reference materials | Lead was complexed with ammonium pyrroldinedithiocarbamate; The limit of detection and the enhancement factor were 0.015 and 76 μg.L⁻¹. |
| Trihalomethanes | [C₆mim][PF₆] | water | The limits of the detection range between 0.1 ng/mL (bromoform) and 0.9 ng/mL (chloroform). |
| Tributyltin and Triphenyltin phenols | [C₆mim][PF₆] | Chinese Medicines | The limit of detection was 0.39 μg.L⁻¹. |
| carbonyl compounds | [C₆mim][PF₆] | water | Enrichment factor is up to 150. HPLC was employed for detection of carbonyl compounds, the limit of detection was in the range of 0.04-0.05 ng.mL⁻¹. |
| cobalt | [C₆mim][PF₆] | water | ETAAS was employed for detection of cobalt, the detection limit was 0.04 μg.mL⁻¹, and the enrichment factor was 120. |
| 2-hydroxy-4-methoxybenzophenone, isoamyl-4-methoxycinnamate, 3-(4-methylbenzylidene)camphor, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, 2-ethylhexyl 4-dimethylaminobenzoate and 2-ethylhexyl 4-methoxycinnamate | [C₄mim][PF₆] | water | HPLC was employed for detection, limits of detection were found in the low μg.L⁻¹ range. |
| lead | Tetradecyl(trihexylphosphonium chloride) | water | 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was used as ligand. ETAAS was employed for detection of lead, its detection limit is 4.5 μg.L⁻¹. |

Table 3. Reviews for single drop microextraction using ionic liquid as acceptor phase
Recently, a novel liquid phase microextraction technology termed dispersive liquid phase micro-extraction (DLME) was developed and validated (Table 4). From the name, it is obviously that it was based on the temperature change or using organic disperser making ionic liquid completely disperse in the aqueous phase and increase the chance of mass transfer into ionic liquid phase, in which the analytes will more easily migrate into the ionic liquid phase because of the much larger contact area than that of conventional single drop liquid micro-extraction, and the ionic liquid was concentrated into one drop by cooling and centrifugation. Experimental indicated that this system could be tuned to a great extent because ionic liquids can be designable and the method does not suffer from the limitations of that in conventional solvent micro-extraction. DLME has been applied to detect trace organophosphorus pesticides [73], fipronil, chlorfenapyr, buprofezin, hexythiazox [74] and mercury [75] with high extraction efficiencies. In general, DLME is more simple and rapid than SDME.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ionic liquid</th>
<th>Sample</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organophosphorus pesticides</td>
<td>[C₆mim][PF₆]</td>
<td>water</td>
<td>HPLC was coupled with analysis; a 70°C of heating and 30min of the centrifugation process were required strongly in order to form a fine dispersive phase and extraction efficiency; serious salting-out effect was also observed.</td>
<td>73</td>
</tr>
<tr>
<td>Fipronil, chlorfenapyr, buprofezin, and hexythiazox</td>
<td>[C₆mim][PF₆]</td>
<td>Water</td>
<td>HPLC was employed for analysis; enrichment factors are in the range from 209 to 276.</td>
<td>74</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>[C₆mim][Ff₂N]</td>
<td>Water</td>
<td>Spectrophotometry was employed for analysis; 4,4’-bis(dimethylamino)-thiobenzophenone was used as chelator of mercury; enrichment factor is about to 18.8.</td>
<td>75</td>
</tr>
<tr>
<td>Sm³⁺, Eu³⁺, Gd³⁺, Dy³⁺</td>
<td>[C₄mim][PF₆]</td>
<td>uranium dioxide powder</td>
<td>Analysis of extracts was performed by HPLC coupled with fluorescence detection; Quantification limits obtained for all of these considered compounds are between 0.1 and 7 ng.L⁻¹.</td>
<td>90</td>
</tr>
<tr>
<td>polycyclic aromatic hydrocarbons</td>
<td>[C₆mim][PF₆]</td>
<td>tap, bottled, fountain, well, river, rainwater, treated and raw wastewater</td>
<td>Zinc was complexed with 8-hydroxyquinoline; The ionic liquid was proposed for the extraction of polycyclic aromatic hydrocarbons.</td>
<td>91</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>1-hexylpyridinium hexafluorophosphate</td>
<td>water and milk</td>
<td>Zinc was complexed with 8-hydroxyquinoline; The ionic liquid was proposed for the extraction of polycyclic aromatic hydrocarbons.</td>
<td>92</td>
</tr>
<tr>
<td>Compound</td>
<td>Ionic Liquid</td>
<td>Matrix</td>
<td>Preconcentration Method</td>
<td>Detection Limits, ng.mL⁻¹</td>
</tr>
<tr>
<td>--------------------------------</td>
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<tr>
<td>Zinc</td>
<td>[C₄mim][PF₆]</td>
<td>urine</td>
<td>Preconcentration of trace levels of zinc as a prior step to determination by flame atomic absorption spectrometry; the limit of detection (3σ) and the enhancement factor were 0.22 μg.L⁻¹ and 71.</td>
<td></td>
</tr>
<tr>
<td>Non-steroidal anti-inflammatory drugs</td>
<td>[C₄mim][PF₆]</td>
<td>urine</td>
<td>The suitability of the proposal is evaluated by means of the determination of non-steroidal anti-inflammatory drugs in urine by liquid chromatography/ultraviolet detection; Limits of detection were in the range from 8.3 ng.mL⁻¹ for indomethacin to 32 ng.mL⁻¹ for ketoprofen.</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>[C₆mim][PF₆]</td>
<td>water</td>
<td>Dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry; The enrichment factor of the method is 67. The detection limit was 7.4 ng.L⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Dichlorodiphenyltrichloroethylene and its main metabolites</td>
<td>[C₆mim][PF₆]</td>
<td>water</td>
<td>The experimental results indicated that the detection limits obtained for p,p’-DDD, p,p’-DDT, o,p’-DDT and p,p’-DDE were 0.24, 0.24, 0.45, 0.24 ng.mL⁻¹, respectively</td>
<td></td>
</tr>
<tr>
<td>Thiophanate-methyl, carbofuran, carbaryl, tebuconazole, iprodione, oxyfluorfen, hexythiazox and fenazaquin</td>
<td>[C₆mim][PF₆]</td>
<td>water</td>
<td>This paper describes a dispersive liquid-liquid microextraction procedure using room temperature ionic liquids coupled to high-performance liquid chromatography with diode array detection capable of quantifying trace amounts of eight pesticides; Limits of detection are between 0.320-4.66μg.kg⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td>[C₄mim][PF₆]</td>
<td>water</td>
<td>The settled phase was injected into HPLC for separation and detection of phenols; The main advantages of the proposed method are high speed, high</td>
<td></td>
</tr>
<tr>
<td>Compound(s)</td>
<td>Ionic Liquid</td>
<td>Solvent</td>
<td>Recovery, good repeatability and environmental friendliness.</td>
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<tr>
<td>Aromatic compounds</td>
<td>[C₆mim][PF₆]</td>
<td>Water</td>
<td>The limits of detection for seven polycyclic aromatic hydrocarbons varied from 0.02 to 0.3 μg.L⁻¹. The enrichment factors were 532 for dicofol and 540 for DDT. Proposed extraction combined with gas chromatography mass spectrometry was a valuable alternative for analysis of dicofol and DDT in environmental water samples within the concentration range 0.005-3.0 μg.L⁻¹. The detection limits were 1.3 ng.L⁻¹ for DDT and 3.2 ng.L⁻¹ for dicofol.</td>
<td></td>
</tr>
<tr>
<td>Dicofol and DDT</td>
<td>1-isoctyl-3-methylimidazolium hexafluorophosphate</td>
<td>Water</td>
<td>Enrichment factor of analytes is 200 and the limits of detection calculated at a signal-to-noise ratio of 3 were in the range of 0.1-5.0 μg.L⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Parathion, Phoxim, Phorate and Chlorpyrifos</td>
<td>[C₆mim][PF₆]</td>
<td>Water</td>
<td>Limits of detection were in the range 0.651-5.44 μg/kg for table grapes and 0.902-6.33 ng.kg⁻¹ for plums.</td>
<td></td>
</tr>
<tr>
<td>Thiophanate-methyl, Carbofuran, Carbaryl, Tebuconazole, Iprodione, Oxynil, Hexthiazox, and Fenazaquin</td>
<td>[C₆mim][PF₆]</td>
<td>Fruit</td>
<td>HPLC was used for detection of five herbicides, their limit of detections were between 0.46 and 0.89 ng.L⁻¹. HPLC-MS was used for detection of triclosan and triclocarb, limits of detection in the range from 0.040 to 0.58 μg.L⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Three triazine and two phenylurea herbicides</td>
<td>[C₆mim][PF₆]</td>
<td>Water</td>
<td>FAAS was employed for detection of lead and cadmium, detection limits are 0.6 μg.L⁻¹ for lead and 0.03 μg.L⁻¹ for cadmium. HPLC-ESI-MS-MS was employed for detection of triclosan and triclocarb, detection limits are in the range from 0.040 to 0.58 μg.L⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺, Cd²⁺</td>
<td>[C₆mim][PF₆]</td>
<td>Saline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triclosan and Triclocarbon</td>
<td>[C₆mim][PF₆]</td>
<td>Water</td>
<td></td>
<td></td>
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</tbody>
</table>

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organophosphorus pesticides 1,3-dibutylimidazolium hexafluorophosphate 121

Enrichment factors are more than 300 times. HPLC was employed for detection of pesticides, Limits of detection were 0.01-0.05 μg.L⁻¹ for four analytes.

V⁵⁺ [C₄mim][PF₆] environment al and biological samples 122

2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was used as ligand. ETAAS was employed for detection of vanadium. The detection limit achieved after preconcentration of 5 mL of sample solution, was 4.8 ng.L⁻¹.

triclosan and triclocarban [C₆mim][PF₆] water HPLC-ESI-MS/MS was employed for detection of triclosan and triclocarban, detection limit is 0.04 and 0.3 μg.L⁻¹. 125

HPLC was employed for detection of triclosan and triclocarban, detection limit is 0.04 and 0.3 μg.L⁻¹.

anthraquinones [C₆mim][PF₆] Radix HPLC was employed for detection of anthraquinones, the limits of detection for all target analytes were ranged from 0.50 to 2.02 μg.L⁻¹. 126

ETAAS was employed for detection of chromium, the limit of detection of the proposed method was 0.07 ng.mL⁻¹.

Cr⁶⁺ [C₆mim][PF₆] lake and tap water 130

Table 4. Reviews for dispersive liquid phase microextraction using ionic liquid as acceptor phase

3.2 Solid phase microextraction

Solid-phase microextraction (SPME) has developed rapidly and it has been widely applied in sample analysis. This is because this simple and solvent-free sample preparation technique, which combines extraction, concentration and sample introduction in one step, is portable, sensitive and convenient to couple with various analytical instruments, especially GC. Almost a dozen different fiber coatings have been commercialized. Among them, the polydimethylsiloxane shows excellent selectivity for non-polar compounds while the polyacrylate coating facilitates the extraction of relatively polar analytes. To date, most of these fiber coatings suffered from limited life span, relatively low operating temperatures in GC applications, and incompatibility with the organic solvents in HPLC mobile phases. In recent years, ionic liquid was widely applied to coating for SPME (Table 4). A typical experimental set-up of headspace SPME mode was illustrated in Fig.3 [79]. The SPME fiber was coated with IL prior to every extraction, the analytes were then extracted and desorbed on the injection port of gas chromatography, and finally the ionic liquid coating on the fiber was washed out with solvents. The coating and washing out of the ionic liquid from the fiber can be finished in a few minutes. Experimental demonstrated that the relatively large
Fig. 3. Schematic diagram of the home-made SPME device: (1) ionic liquid-coated fiber tip; (2) stainless steel needle; (3) silicone rubber O-ring; (4) glass syringe body; (5) moveable stainless steel tubing; (6) stainless steel fiber or polyimide coated fused-silica fiber; (7) localizer.

Viscosity of ionic liquid aided its coating on the SPME fiber and permitted easy washing out after sample injection. On the other hand, the involatility and good thermal stability of the ionic liquid will keep it staying on the fiber when the analytes were thermally desorbed in the injection port of GC, though loss of some of the ionic liquid film occurred due to the simple coating procedure. This proposed disposable ionic liquid-coated fibers show reproducibility comparable with the widely used commercially available SPME fibers, but its sensitivity is lower due to the relatively thin coating. The major advantage of the disposable ionic liquid-coated fiber is the very low cost because only a very low amount of ionic liquid is consumed for each determination. Another advantage of this disposable coating is the carryover was avoided as new fiber coating is used for every determination. However, the detection limits were higher than those obtained using commercially available SPME fibers due to the relative thin film of ionic liquid that can be coated on the fiber. Therefore, this proposed method is only applicable to samples with relatively high levels of analytes. Considering that ionic liquid possess good extractability for various organic compounds and metals ions, and task-specific ionic liquid can be designed and synthesized for selective extraction of target analytes, disposable SPME/LPME coating ionic liquid might has great potential in sample preparation.

Baghdadi group reported a new microextraction with ionic liquid termed cold-induced aggregation microextraction procedure (CIAME) [85]. In this method, very small amounts of 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (as extractant solvents) were dissolved in a sample solution containing Triton X-114 (as an anti-sticking agent). Afterwards, the solution was cooled in the ice bath and a cloudy solution was formed. After centrifuging, the fine droplets of extractant phase were settled to the bottom of the conical-bottom glass centrifuge tube. CIAME is a simple and rapid method for extraction and preconcentration of metal ions from water samples and can be applied for the sample solutions containing high concentration of salt and water miscible organic solvents. Furthermore, this technique is much safer in comparison with the organic solvent extraction. Performance of the technique was evaluated by determination of the trace amounts of mercury as a test analyte in several real water samples. Michler thiokeitone was chosen as a complexing agent. Analysis was carried out using spectrophotometric detection method. Type and amount of IL and the surfactant, temperature and the other parameters were optimized. Under the optimum conditions, the limit of detection of the method was 0.3 ng mL\(^{-1}\) and the relative standard deviation was 1.32% for 30 ng.mL\(^{-1}\) mercury.
### Ionic Liquids: Applications and Perspectives

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ionic liquid</th>
<th>Sample</th>
<th>Remark</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>trihexyltetradecylphosphonium, N-butyl-4-methylpyridinium tetrafluoroborate</td>
<td>Ionic liquid-mediated sol-gel hybrid organic-inorganic materials present enormous potential for effective use in analytical microextraction; Detection limits ranging from 4.9 to 487ng.L⁻¹.</td>
<td>76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td>1-hexadecyl-3-butylimidazolium bromide and 1,3-didodecylimidazolium bromide</td>
<td>GC-MS was employed for the analysis; an aqueous ionic liquid aggregate was used as acceptor; the extraction tube was introduced into the microwave cavity.</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>Esters</td>
<td>polymeric ionic liquids</td>
<td>Water</td>
<td>For the first time polymeric ionic liquids was used as fiber coatings for extraction; GC was employed for analysis; long lifetime and high thermal stability of the polymeric ionic liquid solid phase microextraction coatings may provide them particular advantages in GC–MS applications involving highly selective ester and FAME extractions from complex matrices.</td>
<td>78</td>
</tr>
<tr>
<td>benzenes, toluene, ethylbenzene, and xylenes</td>
<td>[C₆mim][PF₆]</td>
<td>Paint</td>
<td>GC was employed for analysis; the SPME fiber was coated with ionic liquid prior to every extraction; an extraction time of 30min was selected; an obvious salting-out effect was observed well.</td>
<td>79</td>
</tr>
<tr>
<td>nonane, methyl caproate, o-cresol, sec-pheneteryl alcohol</td>
<td>Water</td>
<td>The application of ionic liquids as nonderivatizing solvents for the pretreatment and regeneration of cellulose is a growing area of research; GC was employed for analysis.</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4-Chlorophenol, 3-</td>
<td>[C₈mim][PF₆]</td>
<td>Water</td>
<td>GC was employed for analysis; the partitioning behavior of six imidazolium-based ionic liquid aggregates in water has been studied for the first time. Monocationic and dicationic ionic liquids-aggregates behave as traditional surfactant systems; the obtained partition coefficients show that hydrophobic analytes are preferably extracted with ionic liquids-aggregates compared to more polar analytes.</td>
<td>81</td>
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</table>

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chorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol

Aromatic compounds

[C₄mim]Br, 1-hexadecyl-3-butylimidazolium bromide, 1,3-didodecylimidazolium bromide

Polycyclic aromatic hydrocarbons

[C₄mim][PF₆], 1-benzyl-3-methylimidazolium trifluoromethanesulfonate and 1-methyl-3-phenylpropylimidazolium trifluoromethanesulfonate

Short-chain alcohols, polar and basic amines

1-Ethoxyethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide

Methamphetamine and amphetamine

[Sulfadimethoxine, sulfamethazine, sulfadimethoxin]

[C₄mim][PF₆] water

HPLC was employed for analysis.

Water

Water

nafion membrane was used to support the ionic liquid; GC-MS was employed for analysis.

two ionic liquids contained styrene units that allowed for polymerization and higher carbon content of the bonded silica particles; The sensitivities of the two ionic liquid fibers differing by the anion were similar. Their efficacy compares favorably to that of commercial fibers for polar analytes. The mechanical strength and durability of the polymeric ionic liquid fibers were excellent.

Methamphetamine, sulfadimethoxine, sulfamethazine, sulfadimethoxin

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Table 5. Reviews for solid phase microextraction using ionic liquid as acceptor phase

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>detection; Detection limits are between 0.1 and 0.4 mug.L⁻¹.</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile Bonded ionic liquid polymeric material</td>
<td>114</td>
</tr>
<tr>
<td>CO₂ poly(1-vinyl-3-hexylimidazolium)- bis[(trifluoromethyl)sulfonyl]imide and poly(1-vinyl-3-hexylimidazolium) taurate</td>
<td>118</td>
</tr>
<tr>
<td>polycyclic aromatic hydrocarbons and substituted phenols</td>
<td>119</td>
</tr>
<tr>
<td>lead and nickel</td>
<td>123</td>
</tr>
</tbody>
</table>

4. The combination of analytical technologies with the extraction

Many modern analytical technologies have been applied to couple with microextraction using ionic liquid as extracting media for different analytical purpose such as AAS for metal ions, HPLC, GC and GC-MS for organic compounds. When ionic liquids are employed as medium in various LPME and SPME, HPLC is preferred to GC as separation technique since this ionic liquid is incompatible with GC due to the non-volatility of the ionic liquid. Consequently, the utilizations of ionic liquid in GC are limited to their use as stationary phases, as coaters of the surface of fibers in solid-phase microextraction or as solvents in various liquid phase microextraction including SDME and DLME etc. In order to overcome the problem, some effective attempts have been reported recently in the literatures. For example, Miguel Valcarcel group has successfully developed a new interface for the direct coupling between ionic liquid-SDME and GC-MS [65] (shown in Fig.4). Using this interface, no ionic liquid can reach the GC system dirtying the chromatographic column and a proper volatilization and subsequent transference of the substances to the GC is achieved. Therefore, the advantages of the use of ionic liquids with SDME, avoiding the irreproducibility associated with the use of organic solvents to form the drop, are added to the analytical possibilities of GC-MS. Furthermore, using the interface analytes of an extensive range of polarity/volatility can be determined on account of the fact that no solvent delay is necessary in the detection step. Moreover, Zeng Baizhao group also
Ionic Liquid as Novel Solvent for Extraction and Separation in Analytical Chemistry

Fig. 4. Scheme of the household unit of the interface for the direct introduction of analytes extracted in a drop of ionic liquid into a gas chromatograph.

Fig. 5. The modified sample injection part of GC instrument. The dimension of the homemade tube: outer diameter, 2.0 mm; length, about 15 mm.

provided another scheme to avoid ionic liquid leaking into the chromatographic column (shown in Fig. 5). In the scheme through placing a small glassy tube in the sample injection part, ionic liquid no longer enters into the chromatographic column, thus ionic liquid based microextraction technique can be coupled with GC. To evaluate the proposed method, five chlorobenzene derivatives are used as model. Results show that the chlorobenzenes can be extracted effectively by the ionic liquid and the extractant exhibits good chromatographic...
behavior. The linear ranges are up to 1.5 mg/L and the detection limits range from 0.1 to 0.5 μg/L. As ionic liquids have many unique properties, ionic liquid based microextraction technique coupled with GC has potential application in the detection of pollutants etc. In our laboratory, above two schemes have been investigated too, the results exhibited above two schemes can not avoid the ionic liquid entering into chromatographic column.

5. Effect of solvent properties on the extraction performances

Although several 1-alkyl-3-methylimidazolium hexafluorophosphate room temperature ionic liquids, abbreviated as [Cₙmim][PF₆], have been widely developed as friendly acceptor phase for various extractions in literatures, their application also suffers from many drawbacks. Firstly, these ionic liquids are difficult to be dispersed into aqueous phase and tend to tightly adhere on vessel wall due to high viscosity. The special property results that a long heating process (or mechanical agitation) and extract operation were required strongly in order to obtain good extraction efficiency. Secondly, most of the ionic liquids have relatively high water-solubility, the aqueous phase in the extraction system contains large amounts of imidazolium and hexafluorophosphate. The salting-out will effect on the extraction performance and following analysis in present of high ionic strength for complex samples. Moreover, the imidazolium dissolved in water is of good surface activity, the property may result in producing serious emulsification phenomenon during extraction and prolong phase separation time. In order to resolve above problems, some new ionic liquids have been designed, synthesized and applied to microextraction in the laboratory. For examples, 1,3-diisooctylimidazolium hexafluorophosphate (shown in Fig.6) was developed as a novel solvent for DLPME. In this study, dicofol and its three degradation products were selected as model compounds to optimize the factors relevant to the extraction and evaluate the applicability of the method. Experimental showed the proposed method offers the advantage of simplicity of operation, rapidity, high extraction efficiency and enrichment factor. The temperature-controlled ionic liquid 1-isooctyl-3-methylimidazolium hexafluorophosphate has been developed as novel medium for DLPME. This new mode of LPME with temperature-controlled ionic liquid increases the rapidity due to good hydrophobic property and relatively high melting point of the ionic liquid, the stability of extraction because of the larger volume of extraction solvent that may be used, enhances the sensitivity because of the much larger contact area than that of conventional LPME and SPME. Comparing with room temperature ionic liquid, proposed method has all performance during liquid/liquid and co-precipitation extraction, it can extract various polar or non-polar analyte from aqueous phase into the ionic liquid with high extraction efficiency. Moreover, new extraction can easily avoid the degradation of the pesticide during enrichment step due to no use a long heating time. Thirdly, the incompatibility between the extraction with ionic liquid and GC or GC-MS has become a problem in analytical chemistry due to ionic liquid’s decomposition and leakage. Recently, Zhao group carried out a beneficial attempt to resolve above difficulty. In this study, a new class of stationary phase coatings for SPME based on polymeric ionic liquids is presented. Proposed SPME coatings exhibit exceptional film stability, high thermal stability, reproducible extraction efficiencies, and long lifetimes. Moreover, the fiber coatings were used to extract esters and fatty acid methyl esters from aqueous solution followed by gas chromatographic separation and flame ionization detection. To examine the effect of the matrix on the coatings, extractions were carried out in a synthetic wine solution followed by recovery experiments in two real wine samples.
When carrying out the extractions in aqueous solution, the detection limits for most analytes ranged from 2.5 to 50μg.L⁻¹ whereas lower detection limits were obtained for larger fatty acid methyl esters. Recovery experiments carried out in red and white wines ranged from 70.2 to 115.1% using the poly(ionic liquid) fibers compared to 61.9 to 102.9% using a commercial polydimethylsiloxane fiber of similar film thickness. The structural tuning capability of these new coating materials makes them widely amendable to performing task-specific microextractions.

In selection of solvents for extraction and extractive distillation processes knowledge of the activity coefficients at infinite dilution (γ°) is very important and useful. A large number of works concerns measurements of activity coefficients at infinite dilution of organic solvents in ionic liquids. In separation processes both properties of extractant are important, namely selectivity S and capacity k which can be directly calculated from activity coefficients at infinite dilution for different separation problems. Activity coefficients at infinite dilution are also very helpful for characterizing the behaviour of liquid mixtures, estimation of mutual solubilities, fitting the excess molar energy (GE) model parameters, predicting the existence of an azeotrope, analytical chromatography, calculation of Henry constant and partition coefficients, development of thermodynamic models based on the group contribution methods such as mod. Typical solvents used in separation of aromatic hydrocarbons from aliphatic hydrocarbons are polar components such as sulfolane and N-methylpyrrolidone (NMP). Replacement of these volatile solvents in the separation processes by the nonvolatile ionic liquids can offer advantages such as less complex processes, more simple regeneration of the extractant using techniques as simple as flash distillation or stripping and the environmental protection. Extraction of aromatics from aromatic/aliphatic mixture with ionic liquids is expected to require less process steps and less energy consumption than extraction with conventional solvents due to negligible vapor pressure of ionic liquids. Andrzej Marciniak has made the analysis of cation and anion structure of the ionic liquid and effect of the temperature on the selectivity and the capacity for aliphatics/aromatics and n-hexane/hex-1-ene separation problems [132]. It was found the highest values of selectivity show ionic liquids with less aliphatic character of the anion and the cation, e.g. based on following cations 1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-ethylpyridinium, triethylsulfonium and with –C≡N group in the structure, like [C₅mim]CN. Unfortunately always when the ionic liquid reveals high values...
of the selectivity, the capacity takes low values. Therefore a selection of proper anion and cation is required. The highest values of capacity have \( \text{Tf}_2\text{N}^- \) and \( \text{FeCl}_4^- \) anions. As was shown most of ionic liquids with high values of both selectivity and capacity is based on \( \text{Tf}_2\text{N}^- \) anion. 1-Butyl-4-methyl-pyridinium bis(trifluoromethylsulfonyl)amide have higher values of selectivity than sulfolane and NMP and much higher value of capacity than these two mentioned entrainers for the n-hexane/benzene separation. The highest selectivity for the n-hexane/benzene separation has \([\text{C}_4\text{mim}][\text{SCN}]\) above 4 times higher than for sulfolane with a slightly better capacity. There are a large number of ionic liquids with selectivity and capacity better than sulfolane. A large number of ionic liquids have comparable or better both of selectivity and capacity values than NMP, e.g.: [1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide, triethyl-sulfonium bis(trifluoromethylsulfonyl)-amide, 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide, hexyl-trimethyl-ammonium bis(trifluoromethylsulfonyl)amide, tributylmethylphosphonium methylsulfate, 1-hexyl-oxymethyl-3-methylimidazolium bromide have higher selectivity than sulfolane and much higher value of capacity than these two mentioned entrainers for the n-hexane/benzene separation. The highest selectivity for the n-hexane/benzene separation has \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\) above 4 times higher than for sulfolane with a slightly better capacity. There are a large number of ionic liquids with selectivity and capacity better than sulfolane. A large number of ionic liquids have comparable or better both of selectivity and capacity values than NMP, e.g.: [1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide, triethyl-sulfonium bis(trifluoromethylsulfonyl)-amide, 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide, hexyl-trimethyl-ammonium bis(trifluoromethylsulfonyl)amide, tributylmethylphosphonium methylsulfate, 1-hexyl-oxymethyl-3-methylimidazolium bromide have the highest selectivity of 15.2. For this separation process majority of ionic liquids have selectivity on the level of 2. To improve selectivity and capacity lower temperature is favourable.

From the values of selectivities and capacities, obtained for the large number of ionic liquids, it can be concluded that majority of ionic liquids may replace conventional entrainers applied for the separation processes of aliphatic/aromatic hydrocarbons and alkanes/alkenes.

### 6. Extraction mechanism

There are many investigations concerning extraction mechanism, these mainly are solvent ion pair extraction, ion exchange, and simultaneous combination of these. Among these, ion exchange mode was widely applied to understand the separation performance. In general, the ion exchange mode think metal ions will replace imidazolium cation or the anion combined with the ionic liquid in ionic liquid phase. For example, Dietz’s group has suggested that high distributions in ionic liquid/aqueous system were due to a change in extraction equilibria in comparison to the octanol/aqueous system. In octanol, \( \text{Sr}^{2+} \) is extracted as a strontium nitratoether complex, whereas in ionic liquids, the two axial bound nitrates are substituted with two water molecules bound to the metal ion, and the charged \( \text{Sr}((\text{CE})(\text{H}_2\text{O}))_2^{2+} \) species, where \( \text{CE} \) is dicyclohexano-18-crown-6-ether, is transferred to the ionic liquid phase, the neutrality of the system is maintained through the migration of two imidazolium cations to the aqueous phase for each extracted metal ion. Therefore, the loss of the ionic liquid components in the aqueous phase would be a major limitation for practical applications of ionic liquids in separations and enrichments.\[^{143}\] However, the nature of the ionic liquid is not the only factor which determines the metal extraction pathway, ligand type also has a very important contribution. Professor Jensen has suggested \( \text{La}^{3+} \) was shown to follow an anion exchange mechanism when extracted in an ionic liquid/aqueous system, in contrast to the cation exchange observed in molecular solvents. Here, changing the lipophilicity of the ionic liquid did not change the partitioning mechanism.\[^{144}\] Recently, the ion exchange theory was also applied to explain the extraction performance of amino acids using a room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with dicyclohexano-18-crown-6 system.
The indication of an ion exchange mechanism is the significant leakage of the dialkylimidazolium cation into the aqueous phase on extraction of amino acids-confirmed by monitoring the corresponding UV band. After extraction of amino acids the clear absorption peak of the dialkylimidazolium cation appeared in the spectrum of the aqueous phase at ca. 300 nm. Increasing the initial amino acid concentration in the aqueous phase from \(1\times10^{-3}\) to \(1\times10^{-2}\) mol L\(^{-1}\) results in an increase of the dialkylimidazolium concentration in water after extraction. Clearly this is caused by ion exchange of the dialkylimidazolium cation with the amino acid cation. Thus, the absence of any appreciable anion effect and distribution of dialkylimidazolium cation into water, which accompanies extraction, strongly suggest that extraction of amino acids with DC\(_{18}C_6\) into the ionic liquid is an ion exchange process. However, above all extraction mechanism mode did not consider the extraction functions of the surface charge on the ionic liquid phase and the ionic liquid dissolved in water. In our previous work, the surface tension and Zeta potential of the ionic liquid solution were investigated in detail in order to understand the extraction performance in the room temperature ionic liquid [\(\text{C}_4\text{tmsim}[\text{PF}_6]\)] with CDAA system. It was found the surface tension of the solution decreased with increase of the concentration of [\(\text{C}_4\text{tmsim}[\text{PF}_6]\)] solution, its critical micelle concentration and surface tension of saturated [\(\text{C}_4\text{tmsim}[\text{PF}_6]\)] solution are 1.59×10\(^{-3}\) mol L\(^{-1}\) and 65.95 Nm/m, respectively. The data showed ionic liquid has surface activity, this property allow the ionic liquid to fully interact with the complex or CDAA in aqueous phase and easy to extract the complex into the ionic liquid phase due to micelle extraction function, which is unique property of surfactant. On the other hand, the Zeta potential value of saturated [\(\text{C}_4\text{tmsim}[\text{PF}_6]\)] solution was found to be +2.1 mV. The result showed the double electron layer at the [\(\text{C}_4\text{tmsim}[\text{PF}_6]\)] water interface existed the positive charge. The positive charge will produce strong interaction between Hg-CDAA complex or CDAA species and ionic liquid surface. Above two factors allow ionic liquid has a higher the extraction efficiency than ordinary organic solvent. It should be stated that Zeta potential may be positive or negative value for different ionic liquid, that decide various ionic liquid has different extraction performance. In order to test suggested extraction mechanism, the extraction efficiencies of CDAA in different acidity was researched in detail. The result is very interesting that the order of the extraction efficiency of CDAA is in base > neutral > acid medium. Because CDAA is a weak organic acid, its dissociation product three reagent species in water, these are \(\text{RH}_2\), \(\text{R}-\) and \(\text{R}^2\) respectively, in which CDAA was replaced by \(\text{RH}_2\) in order to simple. In strong base solution, reagent specie is \(\text{R}^2\) mainly, it is easy to extract into ionic liquid due to its strong negative electric charge, the order accord with suggested extraction mechanism \([5]\). Recently, professor Yan Yongsheng suggested a new extraction mechanism by use of ionic liquid-salt aqueous two phase system (shown in Fig.7). Aquous two-phase system consisting of a hydrophilic ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [\(\text{C}_6\text{mim}[\text{BF}_4]\)]) and \(\text{Na}_2\text{CO}_3\), which is a novel, simple, non-toxic and effective sample pretreatment technique coupled with molecular fluorescence spectrophotometry, was developed for the simultaneous separation, enrichment and rapid analysis of roxithromycin. The extraction yield of roxithromycin (ROX) in [\(\text{C}_6\text{mim}[\text{BF}_4]\)]-\(\text{Na}_2\text{CO}_3\) is influenced by the types of salts, concentrations of \(\text{Na}_2\text{CO}_3\) and [\(\text{C}_6\text{mim}[\text{BF}_4]\)], as well as the extracting temperature. The mechanism of ionic liquid-salt aqueous two-phase system formation was discussed by hydration theory, and the extraction mechanism of the [\(\text{C}_6\text{mim}[\text{BF}_4]\)]-salt was investigated by FT-IR spectroscopy and UV-vis spectroscopy. The results demonstrate that no chemical (bonding) interactions are observed between ionic liquid and roxithromycin (ROX), while the nature properties of the ROX are not altered \([146]\).
It should be pointed the extraction performance of the ionic liquids are very complex due to its complex solvent characteristics, the theory modes concerning extraction mechanism need improve and confirmed by reliable experiments technologies in the future.

Fig. 7. The schematic diagram of separating ROX in ionic liquid-salt aqueous two phase system

7. References


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This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

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