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Ionic liquid-based microextraction: A sample pretreatment technique for chromatographic analysis

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ABSTRACT

Ionic liquids (ILs), also known as molten salts with low melting points, are receiving an upsurge of interest as green solvents and form an attractive area of research. Within the last few years, research and applications of ILs as extraction solvents in sample pretreatment prior to chromatographic analysis have expanded tremendously. This review presents an overview of IL microextraction-based sample pretreatment techniques for high performance liquid chromatography (HPLC) and gas chromatography (GC).

1. Introduction

High performance liquid chromatography (HPLC) and gas chromatography (GC) are widely used analytical techniques for the analysis of chemicals in biological, pharmaceutical, food, and environmental fields. Nowadays, the situation often encountered for the analysts is that they have to analyze trace components in complex matrices such as food, wastewater, soil, urine, solid waste, blood, etc. Target analytes usually exist in very low concentrations (usually in the range of μg/L to mg/L) and the number of matrix components at similar or higher concentration level may be enormous. However, in a typical HPLC or GC run only about a dozen analytes can be separated. Therefore, in most cases it is necessary to eliminate matrix interferences before chromatographic analysis. At present, different sample pretreatment techniques such as liquid-liquid extraction (LLE), liquid phase microextraction (LPME), solid phase extraction (SPE) and solid phase microextraction (SPME) were usually used for this purpose [1,2]. However, most sample pretreatment methods involve the use of organic solvents. Besides supercritical fluid and subcritical water, organic solvents were the only choice for a long time. These organic solvents are usually volatile, flammable and toxic to the operators.

Ionic liquids (ILs) [3-5], sometimes called molten salts, are liquids entirely composed of organic cations and inorganic or organic anions at or close to the room temperature. ILs are regarded as potentially environmentally-benign solvents because they have no-detectable vapor pressure. They also have the characteristics of high thermal stability, non-flammability and good solubility for inorganic and organic compounds. Furthermore, their chemical and physical properties (melting point, density, water immiscibility, viscosity, etc.) can be easily modified by suitable combination of different cations and anions. Therefore, ILs have been extensively investigated as replacements for conventional organic solvents in extraction processes. Several excellent reviews have compiled the applications of ILs in analytical chemistry [6-15].

In this work, the following shorthand notations are used to describe IL cations, where subscripts refer to the number of carbons in the alkyl chain: 1-butyl-3-methylimidazolium ($[C_4mim]^+$), 1-hexyl-3-methylimidazolium ($[C_6mim]^+$) and 1-octyl-3-methylimidazolium ($[C_8mim]^+$). Anions involved herein include: hexafluorophosphate ($[PF_6]^-$), tetrafluoroborate ($[BF_4]^-$) and bis(trifluoromethanesulfonyl)imide ($[NTf_2]^-$). Therefore, $[C_4mim][PF_6]$ indicates the IL 1-butyl-3-methylimidazolium hexafluorophosphate.

Generally, the synthesis of ILs can be divided into two sections: formation of the desired cation, usually through a quaternization reaction on a nitrogen atom, whether it is a pyridine, an imidazole, or an amine, and commonly done with an alkyl halide; and then followed by anion metathesis to pair the cation with the desired anion. For the sake of easy understanding, chemical structures of common ILs are shown in Figure 1.

Compared with conventional exraction, the main advantage of microextraction is extremely little solvent and sample consumption. Therefore, microextraction methods may be the direction for future development of sample pretreatment for chromatographic analysis. ILs show good compatibility with C18 column, but ILs are not compatible with GC and ion-exchange column due to their nonvolatility and ion states. So, to the best of our knowledge, there is no reported literature on the applications of ILs to sample pretreatment for ion chromatography (IC). So, in this work, the latest progress of the

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applications of ILs-based microextraction to sample pretreatment for HPLC and GC analysis are reviewed. The combinations of IL-based microextraction methods and other instruments such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and UV-vis spectrometry are not discussed because they are outside the scope of this review.

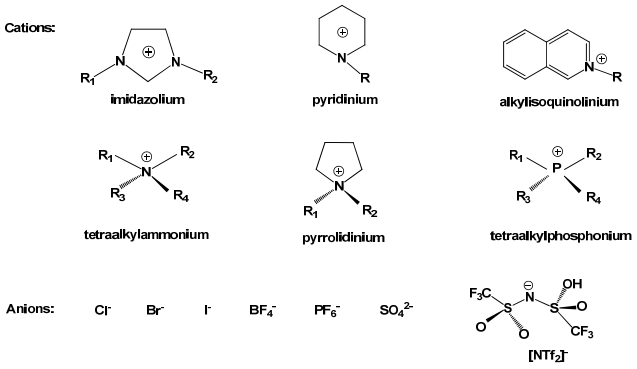

Figure 1. Chemical structures of cations and anions of ILs.

2. Liquid phase microextraction (LPME)

The continuous quest for novel sample pretreatment techniques has led to the development of new methods, whose main advantages are their speed and negligible volume of solvents used. The most recent trends include LPME, a miniaturization of the traditional liquid-liquid extraction method, where the solvent to aqueous ratio is greatly reduced. Several methods including single drop microextraction (SDME) [1,2], dispersive liquid-liquid microextraction (DLLME) [16,17] and hollow fiber supported liquid phase microextraction (HF-LPME) [1,2] evolved from this approach. The hydrophobic character of some ILs makes them useful for LPME.

2.1. IL-based single drop microextraction (IL-SDME)

SDME is an approach evolved from LPME in which the extraction phase is a drop of solvent, usually suspended in the needle of a syringe, direct immersed in the sample solution (DI-SDME) or in close contact with its headspace (HS-SDME) [2]. Generally, in SDME a polytetrafluoroethylene (PTFE) tube was fitted to the blunt needle tip, maximizing the contact area between the drop and the needle tip.

SDME is a simple, inexpensive, fast and effective sample pretreatment technique. Since Liu and coworkers [18] proposed ILs as solvents in SDME for the extraction of polycyclic aromatic hydrocarbons (PAHs), their use has received more attention and their extractability has been fully investigated [19-37]. In the past few years, many reported works have described the applications of IL-SDME combined with HPLC for the extraction and analysis of free benzophenone-3 [19], dichlorodiphenyltrichloroethane (DDT) and its metabolites [20], aromatic amines [21], phenols [22-24], chlorobenzenes [25,26], chlorinated anilines [27], formaldehyde [28], mercury species [29] and UV filters [30] from various matrices. Compared with conventional organic solvents, ILs possess higher viscosity that allows ILs to form a larger volume drop and survive for a long extraction time, resulting in higher extraction efficiencies and enrichment factors.

However, when ILs are employed as extractants in SDME, HPLC is preferred to GC as separation technique, since IL-based SDME is incompatible with GC due to the nonvolatility of ILs. In order to overcome this obstacle, efforts have been made in the last few years to explore the feasibility to couple the IL-based SDME with GC [31-38]. Recently, Aguilera-Herrador and coworkers [31], for the first time, designed a new removable interface permiting the direct injection of the extracted analytes into the GC-MS system, while preventing the IL from entering the column. The interface is based on a removable unit packed with cotton, which is used to trap the IL. In subsequent works from the same research group, the proposed device was also applied to the determination of benzene, toluene, ethylbenzene and xylene isomers (BTEX) [32] and trihalomethanes [33,34] in water samples. However, this device was complicated and the operation was inconvenient. In response to these questions, several groups have developed new approaches. Zhao *et al*. [35] proposed a simple method for the direct use of IL-based SDME prior to GC through the improvement of the injection system. They enlarged the upper diameter of the split inlet liner in which some glass wool was placed in order to mix the analytes well and retain the fall-off IL. Thus, the IL-based SDME could be coupled with GC. In subsequent research, Zhao and coworkers [36] extended their work. They just placed a small glass tube in the sample-injection part to incept the IL microdrop when it was not successfully retracted. When the small tube was full, the IL was taken out with a syringe or the small tube was replaced, which was easy to conduct.

Chisvert *et al*. [37] introduced a simple and commercial readily-available approach for the combination of IL-based SDME and GC. The approach is based on the thermal desorption (TD) of the analytes from the IL droplet to the GC system by using a commercially available TD system. After extraction, the IL droplet was placed inside a 20 mm glass Pyrex tube, which was placed inside a 187 mm commercial TD glass tube that was fitted with glass wool. The whole device containing the IL droplet was manually placed inside the commercial TD system. Thus, the compounds extracted in the IL droplet are thermally desorbed and transferred to GC thereafter. Moreover, the approach allows larger volumes of IL to be used without the need of disassembling the inlet, and thus avoiding equilibration times, which allows increasing the sample throughput within a working day. On the other hand, as no extractant reaches the GC system, no solvent delay is necessary in the detection step, thus allowing its acquisition from the first moment, which enables highly volatile substances to be determined with small retention times. Table 1 summarizes the applications of IL-SDME prior to HPLC or GC analysis.

Although ILs are very suitable for HS-SDME of volatile and semivolatile compounds, one disadvantage of IL-based DI-SDME is the instability of suspending of the IL droplet. Besides, ILs-SDME is still a time-consuming process.

2.2. IL-based dispersive liquid-liquid microextraction (IL-DLLME)

DLLME was introduced by Rezaee *et al*. in 2006 [39]. It is based on the use of a ternary component solvent system (i.e., sample solution, disperser solvent, and extractant). In this method, the appropriate mixture of extraction solvent and disperser solvent is injected into sample solution by syringe, rapidly. Thereby, cloudy solution is formed. Figure 2 depicts the general procedure of DLLME. Compared with SDME, the principal advantage of DLLME is that the surface area between the extractant phase and the aqueous phase is extremely large, so the equilibrium state is achieved quickly and, therefore, the extraction time is very short [40]. After the centrifugation of the cloudy solution, the determination of analytes in extraction phase can be performed by instrumental analysis. Rapidity, high enrichment factor, simplicity of operation, and low cost are some of the advantages of this method. Several recent

reviews have summarized the principles and applications of DLLE [2,16,17].

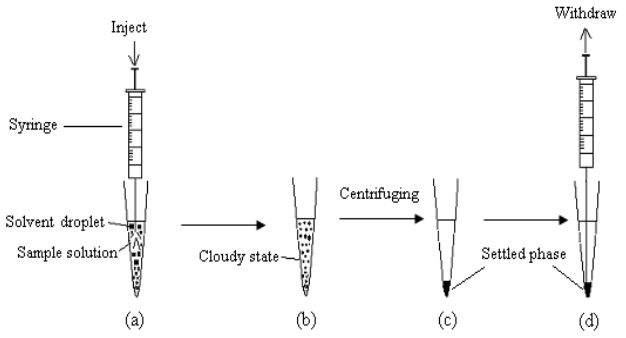

Figure 2. Different steps in DLLE: (a) injection of the mixture of disperser solvent and extractant; (b) dispersion of dispersive solvent and extractant; (c) after centrifuging and (d) the settled phase was collected with a microsyringe. Adapted from [40].

Recently, several papers have reported the IL-based DLLE (IL-DLLME), i. e., replacing conventional extractant with IL, as a novel sample pretreatment technique prior to chromatographic analysis [41-56]. He and coworkers [41,42] reported IL-DLLME for the preconcentration of organophosphorus pesticides from water and fruit samples. Using a similar protocol, pesticides in bananas [43] and table grapes and plums [44], heterocyclic insecticides [45], PAHs [46], carbamates [47] in water and fruit samples and pesticides and metabolites in soils [48] were enriched and analyzed by HPLC. In 2009, Cruz-Vera and co-workers [49] developed a one-step in-syringe IL-DLLME. This novel method avoids the centrifugation step, typically off-line and time consuming, opening-up a new horizon on DLLME automation.

The extraction process consists of three well-defined steps, namely: sample loading, extraction and phases separation. At the beginning, a specific volume of sample solution (typically 10 mL) is aspirated in the 10 mL-syringe by means of a PTFE tubing adapted to the tip of the syringe. Then, 1000 µL of the extraction mixture, containing 720 µL of disperser solvent (methanol) and 280 µL of the extractant ($[C_4mim][PF_6]$), is sprayed by using the 1000-µL glass syringe, a cloudy solution being immediately formed. Later on, the plunger of the 10 mL-syringe is slowly moved to the initial point allowing the recovery of the IL from the wall and the lower part of the syringe while the urine sample is removed from the unit. Finally, the IL phase containing the target analytes can be easily recovered from the syringe tip.

However, all these IL-DLLME methods also involve the use of volatile organic solvents such as methanol and acetone (disperser solvents). To overcome this problem, the binary solvent system-based DLLE, in which the extraction system only consists of IL and water, i.e., no disperser solvent is required, has been developed. Our group [50] used this approach coupled with HPLC for the preconcentration and analysis of aromatic amines in water. In this method, a 1.8-mL portion of the sample solution and 50 µL of $[C_4mim][PF_6]$, as extracting solvent, were placed in a 2.2-mL glass test tube with conical bottom. One milliliter of the above mixture was withdrawn into a 1-mL syringe. Then the syringe plunger was pushed rapidly to inject the contents into the remaining solution. The above procedure was repeated twice in order to entirely disperse IL into the aqueous phase. The cloudy mixture was centrifuged. The IL phase was injected directly into the HPLC.

Zhou and coworkers introduced a temperature-controlled IL-DLLME for the extraction of pyrethroid pesticides [51], chlorotoluron, diethofencarb and chlorbenzuron [52], organophosphorus pesticides [53] and DDT and its metabolites [54] in water. In this method, the mixture of IL and water sample was heated in a glass tube. The IL was then dispersed completely into the aqueous solution under the drive of temperature. The tube was, thereafter, cooled with ice water and phase separation of IL from water was realized by centrifuging. The IL phase was diluted for HPLC analysis. Using the similar procedure, aromatic amines [55], anthraquinones [56], hexabromocyclododecane diastereomers [57], chloro benzenes [58] and DDT and Dicofol [59] were determined by HPLC or GC from various matrices.

Yao *et al.* [60] introduced a novel IL-DLLME using an in situ metathesis reaction to form a water-immiscible IL extraction phase. Briefly, a hydrophilic IL was added into solution. The IL was completely dispersed and dissolved into the aqueous solution after gentle shaking. An aqueous $LiNTf_2$ solution was then added and resulted in the formation of a turbid solution with fine IL microdroplets which greatly increases the surface area between IL and water resulting in high enrichment factors. After shaking for 30 s, the turbid solution was centrifuged for 5 min at a rate of 3400 rpm. The upper aqueous solution was removed, and the IL residue enriched with analytes was withdrawn into a syringe and injected into HPLC. Table 2 collects the applications of IL-DLLME combined with HPLC or GC.

Compared with conventional extraction techniques, the advantages of IL-DLLME are simplicity of operation, rapidity, high enrichment factor, and very short extraction time (a few seconds). However, the selectivity of IL-DLLME is rather poor, which would lead to serious interferences from complex matrix co-extractives.

2.3. Hollow fiber supported ionic liquid membrane microextraction (HF-ILMME)

Hollow fiber supported liquid membrane microextraction (HF-LMME) or called hollow fiber supported liquid phase microextraction (HF-LPME) is a novel miniaturized sample pretreatment technique that has gained extensive attention in analytical chemistry [2]. In HF-LMME, analytes were extracted from an aqueous sample (also called donor solution) through a water-immiscible solvent membrane immobilized in the pores of the hollow fiber and finally, into the acceptor solution placed inside the lumen of the hollow fiber. As discussed above, the major problem of SDME is that the droplet suspended on the needle tip of microsyringe is easily lost. Therefore, HF-LMME is a good alternative.

Peng *et al.* [61] used IL $[C_8MIM][PF_6]$ as membrane solvent for HF-LPME, in which a 5.0 cm-long polypropylene hollow fiber was immersed in IL for 10 min to immobilize the IL in the pores of the hollow fiber. This hollow fiber was taken out and its outside and inside were washed five times with water. Then it was mounted onto the needle tip of the microsyringe holding acceptor solution (sodium hydroxide solution, pH=13). Thereafter, the plunger of the microsyringe was depressed to flush out the acceptor solution to wash and fill the lumen of the hollow fiber. Afterwards, the other end was sealed with heated tweezers and the prepared hollow fiber with the microsyringe was immersed into the sample solution. Recently, this technique was also applied to the extraction of aliphatic and aromatic hydrocarbons [62] and sulfonamides [63] in environmental water prior to GC or HPLC analysis.

High selectivity, sensitivity, efficient sample clean-up, and low organic solvent consumption are the main advantages of HF-LMME compared to most traditional extraction techniques. However, this method also belongs to a time-consuming process because of low mass transfer rate.

Table 1. Reported applications using IL-SDME as sample pretreatment techniques for HPLC and GC analyses.

Target analytes/matrix	Sampling mode	IL	Analytical method	Limits of detection (μg L^{-1})	Enrichment Factor	Recovery (%)	Reference
PAHs/water	DI-SDME	$[C_8MIM][PF_6]$	HPLC-fluorescence Detection (FLD)	NR[a]	42-166	NR	[18]
Benzophenone-3/human urine	DI-SDME	$[C_6MIM][PF_6]$	HPLC-DAD	1.3	23	NR	[19]
DDT and its metabolites/water	HS-SDME	$[C_4MIM][PF_6]$	HPLC-UV–vis detection (UVD)	0.05–0.08	NR	86.8-102.6	[20]
Aromatic amines/water	HS-SDME	$[C_4MIM][PF_6]$	HPLC-UVD	0.09–0.38	13.7-116.3	81.9-99.1	[21]
Phenols/water	HS-SDME	$[C_4MIM][PF_6]$	HPLC-UVD	0.3–0.5	17.2-160.7	89.4-114.2	[22,23]
4-Nonylphenol and 4-*tert*-octylphenol /water	DI-SDME	$[C_6MIM][PF_6]$	HPLC-FLD	0.3-0.7	130-163	90-113	[24]
Chlorobenzenes/water	HS-SDME	$[C_4MIM][PF_6]$	HPLC-photodiode array detection (PAD)	0.102-0.203	NR	61-121	[25]
Chlorobenzenes/water	Microwave-assisted HS-SDME	$[C_6MIM][PF_6]$	HPLC-PAD	0.016-0.039	NR	82-106	[26]
Chlorinated anilines/water	HS-SDME	$[C_4MIM][PF_6]$	HPLC-diode array detection (DAD)	0.5-1.0	NR	81.9-99.6	[27]
Formaldehyde/shiitake mushroom	DI-SDME	$[C_8MIM][PF_6]$	2,4-Dinitrophenylhydrazine as derivative, HPLC-DAD	5	NR	80-102	[28]
Mercury species/water	DI-SDME	$[C_6MIM][PF_6]$	HPLC-PAD	1.0-22.8	3-31	83-123	[29]
UV filters/water	DI-SDME	$[C_6MIM][PF_6]$	HPLC-DAD	0.06-0.19	8-98	92-115	[30]
Dichloromethane, *p*-xylene, *n*-undecane/water	HS-SDME	$[C_4MIM][PF_6]$	GC-mass spectrometry (MS)	5.6-15.6	NR	NR	[31]
BTEX/ water	HS-SDME	$[C_8MIM][PF_6]$	GC-MS	22×10^{-3}-91×10^{-3}	NR	88.9-103.1	[32]
Trihalomethanes/water	HS-SDME	$[C_8MIM][PF_6]$	GC-MS	0.5-0.9	NR	91.6-101.7	[33]
Trihalomethanes/water	HS-SDME	$[C_8MIM][PF_6]$	Room temperature GC-ion mobility spectrometry (IMS)	0.10-0.91	NR	NR	[34]
Phenols/water	HS-SDME	$[C_8MIM][PF_6]$	GC-flame ionization detection (FID)	0.1-0.4	35-794	81-111	[35]
Chlorobenzene derivatives/water	HS-SDME	$[C_8MIM][PF_6]$	GC-FID	0.1-0.5	41-127	88.9-110	[36]
Chlorobenzenes/water	HS-SDME	$[C_6MIM][PF_6]$	GC-MS	1×10^{-3}-4×10^{-3}	NR	90-115	[37]
Organochlorine pesticides/soil	HS-SDME	$[C_4MIM][PF_6]$	GC-^{63}Ni ECD	0.1-0.5 ng/g	NR	NR	[38]

[a] Not reported.

3. Solid phase microextraction (SPME)

SPE is an increasingly useful sample pretreatment technique. In SPME, analytes are extracted from aqueous or gaseous samples onto a solid polymeric fiber. Finally, the fiber is transferred to a GC or to the HPLC interface for analysis. The main advantage of SPE is simple to use, relatively fast and can be automated and coupled on-line to analytical instrumentation. However, the main problem commonly encountered with SPME is the sample carry-over effects between runs.

Recently, because of their relative high viscosity and thermal stability, ILs have been used in SPME technique, where ILs are adsorbed or chemically bonded to fibers [64-80]. Liu *et al*. [64] demonstrated the IL $[C_8mim][PF_6]$ can be physically absorbed on the surface of the fused-silica fiber or stainless steel wire. The resulting fiber demonstrates good reproducibility comparable with the widely used polydimethylsiloxane (PDMS) fiber for the analysis of BTEX in paint samples, but its sensitivity is lower due to the relatively thin coating. In order to overcome this problem, Hsieh *et al*. [65] utilized a Nafion membrane to increase the amount of IL absorbed on the fiber. Nafion is a proton-exchange polymer with side chains terminating in sulfonic acid. It would increase the amount and stability of IL absorbed on the fiber surface through the electrostatic interaction between IL and the Nafion membrane. The fiber was used to extract PAHs from aqueous solution prior to GC-MS analysis. Huang and coworkers [66] introduced an alternative SPME technique, in which fused-silica capillaries were etched with ammonium hydrogen difluoride prior to coating with IL $[C_4mim][PF_6]$. The resultant fiber exhibited best extraction ability compared with the Nafion membrane-supported IL-SPME fiber and PDMS-coated SPME fiber. A comparison of extraction efficiency of the proposed fiber and that of commercial PDMS-coated SPME fiber is shown in Figure 3. In these cases, the fiber was re-coated after each desorption step. Therefore, one advantage of this disposable coating is the sample carry-over was avoided. However, the main disadvantage is the contamination of the GC injection liner resulting from the ILs dripping into the injection port.

To overcome this problem, in 2008, Zhao *et al*. [67] used polymeric ionic liquids (PILs) as a novel class of stationary phase coatings for SPME. The synthesis procedure for PILs is shown in Figure 4. The polymerization of IL monomers produces materials that can be coated as thin films on supports while resisting large viscosity drops with elevated temperatures and exhibiting exceptional thermal stability and long lifetimes. Finally, the polymeric IL-based fibers showed exceptional highly reproducible extraction efficiencies for esters and fatty acid methyl esters in both an aqueous and synthetic wine solutions. López-Darias *et al*. [68] used the PIL poly (1-vinyl-3-hexadecylimidazolium) *bis*[(trifluoromethyl) sulfonyl]imide as a coating material in SPME. The resultant fiber was applied to extraction of PAHs and substituted phenols in water in a direct immersion mode. The PIL fiber shows no obvious decrease in its performance after 50 non-consecutive extractions.

Table 2. Applications of IL-DLLME sample pretreatment for HPLC and GC analyses.

Analytes/matrix	Sampling mode[a]	IL	Disperser solvent	Instrument	Limits of detection	Enrichment Factor	Recovery (%)	Reference
Organophosphorus pesticides/water	TSS	$[C_8MIM][PF_6]$	Methanol	HPLC-UVD	0.1-5.0 μg L^{-1}	>200	87.3-117.6	[41]
Organophosphorus pesticides	TSS	$[C_4C_4IM][PF_6]$	Methanol	HPLC-UV/Vis	0.01-0.05 μg L^{-1}	309-335	91.3-109.1	[42]
Pesticides/banana	TSS	$[C_6MIM][PF_6]$	Methanol	HPLC-DAD	0.320-4.66 μg kg^{-1}	NR[f]	53-97	[43]
Pesticides/table grape and plum	TSS	$[C_6MIM][PF_6]$	Methanol	HPLC-DAD	0.902-6.33 μg kg^{-1}	NR	58-106	[44]
Heterocyclic insecticides/water	TSS	$[C_6MIM][PF_6]$	Methanol	HPLC-DAD	0.53-1.28 μg L^{-1}	209-276	79-110	[45]
PAHs/water	TSS	$[C_8MIM][PF_6]$	Acetone	HPLC-FLD	0.03-0.5 ng L^{-1}	301-346	30.4-103.3	[46]
Carbamate insecticides/water and fruit	BSS	$[C_4MIM][PF_6]$	NU[c]	HPLC-UV	2.0-40.0 μg L^{-1}	10-25	81-118	[47]
Pesticides and metabolites/soil	TSS	$[C_6MIM][PF_6]$	Methanol	HPLC-FLD	0.02-27.07 ng g^{-1}	NR	82-119	[48]
Non-steroidal anti-inflammatory drugs/urine	TSS	$[C_4MIM][PF_6]$	Methanol	HPLC-SWPM[d]	8.3-32.0 μg L^{-1}	73.7-84.6	99.6-107.0	[49]
Aromatic amines/water	BSS	$[C_4MIM][PF_6]$	NU	HPLC-VWD[e]	0.45-2.6 μg L^{-1}	31-269	92.4-106.4	[50]
Pyrethroid pesticides/water	BSS	$[C_6MIM][PF_6]$	NU	HPLC- UV	0.28-0.60 μg L^{-1}	NR	76.7-135.6	[51]
Chlorotoluron, diethofencarb and chlorbenzuron/water	BSS	$[C_6MIM][PF_6]$	NU	HPLC-UVD	0.04-0.43 μg L^{-1}	NR	86.3-106.5	[52]
Organophosphorus pesticides/water	BSS	$[C_6MIM][PF_6]$	NU	HPLC-UD	0.17-0.29 μg L^{-1}	50	88.2-103.6	[53]
DDT and its metabolites/water	BSS	$[C_6MIM][PF_6]$	NU	HPLC-UD	0.24-0.45 μg L^{-1}	50	87.4-110.0	[54]
Aromatic amines/water	BSS	$[C_6MIM][PF_6]$	NU	HPLC-UD	0.17-0.49 μg L^{-1}	NR	92.2-119.3	[55]
Anthraquinones/Radix et Rhizoma Rhei	TSS	$[C_6MIM][PF_6]$	Methanol	HPLC-DAD	0.50-2.02 μg L^{-1}	174-213	95.2-108.5	[56]
Hexabromocyclododecane diastereomers/water	BSS	$[C_6MIM][PF_6]$	NU	HPLC-MS	0.1 μg L^{-1}	NR	77.2-99.3	[57]
Chlorobenzenes/water	BSS	$[C_4MIM][PF_6]$	NU	HPLC-DAD	0.05-0.1 μg L^{-1}	187-298	91.0-111.0	[58]
DDT and dicofol/water	TSS	$[C_8MIM][PF_6]$	Methanol	GC-MS	1.3-3.2 ng L^{-1}	532-540	96-106	[59]
Aromatic compounds/water	BSS	$[C_4MIM]Cl$ [b]	NU	HPLC-UVD	0.02-34.5 μg L^{-1}	184-935	84-115	[60]

[a] TSS: Ternary solvent system; BSS: Binary solvent system.
[b] $LiNTf_2$ as an ion-exchange reagent.
[c] Not used.
[d] SWPM: Single wavelength photometer
[e] VWD: Variable wavelength detection
[f] Not reported.

Wanigasekara and coworkers [69] reported that the PIL-bonded silica particles could be coated on SPME fibers to be used for the extraction of small and polar molecules such as short amines, short-chain alcohols, acetonitrile, and acetone. He *et al*. [70] presented a new SPME technique using IL, in which the IL-based SPME fiber was prepared by fixing IL through cross-linkage of IL impregnated silicone elastomer on the surface of a fused silica fiber. The resulting fiber was applied to the forensic headspace determination of methamphetamine (MAP) and amphetamine (AP) in human urine samples. The extraction efficiency of the fiber did not change after more than 100 extractions.

Shearrow and coworkers [71] employed IL-mediated sol-gel materials for in-tube SPME (also called capillary microextraction, CME). In this technique, the sorbent coating is placed on the capillary inner wall; analytes are extracted by passing the sample through the coated capillary. The IL-mediated sol-gel coatings provided higher sensitivity compared to analogous sol-gel coatings prepared without IL and the extraction efficiency of the IL-mediated sol-gel coatings depended on its porosity and the nature of the organic polymer and the precursor. A significant advantage of in-tube SPME over traditional fiber SPME is that the sorbent coating is protected against mechanical damage during operation because it is secured on the inner wall of a capillary.

Zhao *et al*. [72-73] synthesized two PILs, poly(1-vinyl-3-hexylimidazolium) *bis*[(trifluoromethyl)sulfonyl]imide [poly (VHIM-NTf_2)] and poly(1-vinyl-3-hexylimidazolium) taurate [poly(VHIM-taurate)]. The two PILs were employed as sorbent coatings in SPME for the selective extraction of CO_2 and exhibited two different types of mechanisms, namely, physical sorption by the poly(VHIM-NTf_2) coating and carbamate formation by the poly(VHIM-taurate) coating. In comparison to the commercial carboxen SPME fiber, similar extraction efficiency of CO_2 was achieved using the poly(VHIMNTf_2) PIL fiber at high CO_2 pressure, despite the fact that the carboxen fiber possessed a much larger film thickness.

4. Conclusion

ILs have been widely applied in sample pretreatment techniques due to their attractive properties. While this field continues to progress, some problems should be noted. For example, compared with conventional organic solvents, ILs also have their own drawbacks: (1) imidazolium-based ILs are the most commonly used in extraction processes, but they have significant absorption in the entire UV region, which can result in serious background interference for HPLC-UV analysis; (2) at present, the anions of hydrophobic ILs commonly used in extraction fields are PF_6^- and BF_4^-.

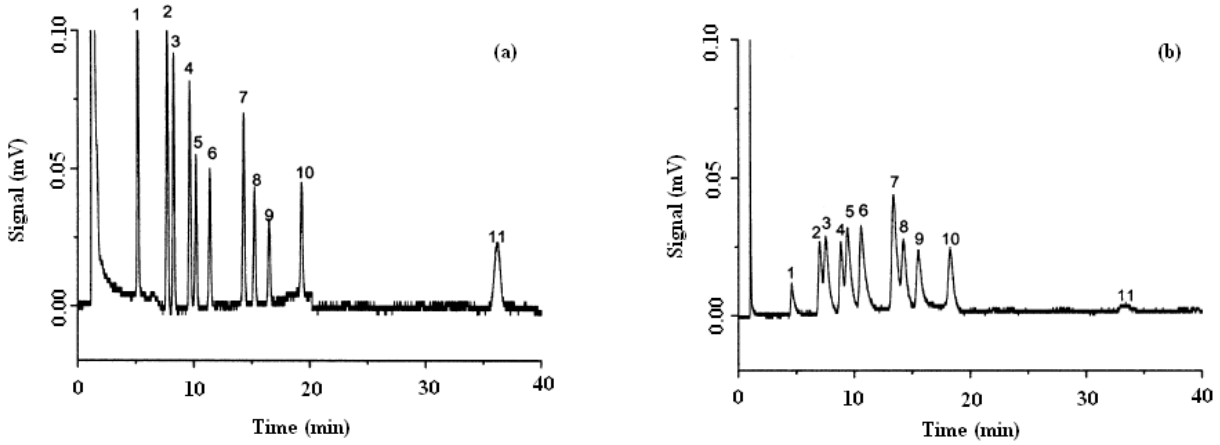

Figure 3. Comparison of extraction efficiency of [C_4mim][PF_6] coating on the etched fused-silica fiber and that of commercial PDMS-coated SPME fiber. Peaks: (1) Naphthalene, (2) 2-methylnaphthalene, (3) 1-methylnaphthalene, (4) azulene, (5) biphenyl, (6) diphenyl methane, (7) acenaphthene, (8) acenaphthylene, (9) dibenzofuran, (10) fluorene and (11) phenanthrene. Adapted from [66].

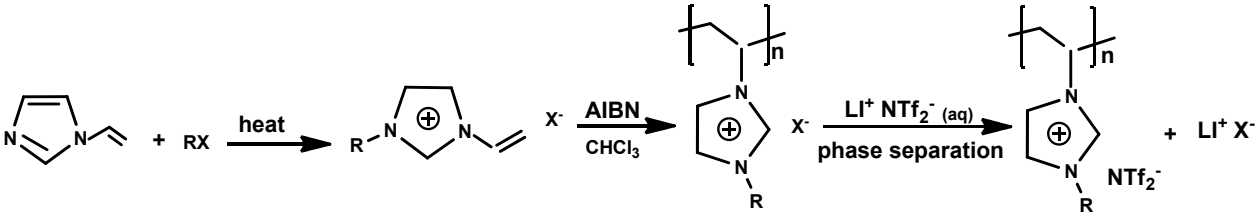

Figure 4. Synthesis of PILs. Adapted from [67].

Unfortunately, these fluoride-containing anions were proven to produce HF in contact with moisture, which may damage glassware and steel parts [81,82]; (3) ILs are not compatible with ion-exchange column. These problems limit the applications of the IL-based microextraction techniques. The polymeric IL-based SPME solves some of these problems and will be a promising development direction. Finally, other efforts can be made to further develop the IL-based on-line (micro) extraction techniques and devices.

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