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Developments/Application of Ionic Liquids/Poly Ionic Liquids in Magnetic Solid-Phase Extraction and Solid Phase Microextraction

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Abstract: This review gives a survey on the latest most representative progress concerning ionic liquids and poly ionic liquids in magnetic solid phase extraction, from their fundamental Approaches to their developments and applications. It also highlights the recent advancements in the ionic liquid and poly ionic liquid in magnetic solid phase extraction and Solid phase microextraction.

Keywords: Ionic Liquid, Poly (Ionic Liquid), Magnetic Solid-Phase Extraction, Developments/Application

1. Introduction

Ionic liquids (ILs) are a type of organic salts possess special physicochemical properties, like good stability and hydrophobic properties [1], [2]. These non-molecular compounds exhibit melting points below 100°C, low to negligible vapor pressure at room temperature, high chemical stability and wide electrochemical windows [3], [4]. They also have been pointed out as green solvents because they do not generate volatile organic compounds and are hydrolytically stable. The important properties of ionic liquids (ILs) include ex-tremely low volatility, non-flammability, high thermal stability, allowing fine-tuning of the ILs properties for specific applications [5], [6]. Their structures can be easily modified by incorporating different functional groups to the cationic/anionic moieties [7].

In spite of the evolution of analytical instrumentation, complex sample analysis or extraction is still a problem without a sample pretreatment, so it concerned as the most important parts of the whole analysis process [8]. The development of new materials as solid phase extraction adsorbent in sample preparation has been widely exploited to obtain more selective materials with higher adsorption capacity [9], [10]. Polymeric ionic liquids (PILs) are a novel class of materials that combines the properties of ILs and polymers. These compounds have generated intense interest in a variety of areas ranging from material synthesis to separation science [11].

Solid phase extraction (SPE) is the most widely used as an a great separation/preconcentration technique, mainly due to the variety of different materials employed as sorbents [12]. The solid phase extractants are distinguished by fast kinetic properties, as well as by the simplicity of their preparation.

Anchoring IL to magnetic materials for example, can combine the unique properties of IL with the advantages of magnetic materials. Zhang et al. first used IL-modified magnetic nanoparticles in mixed hemimicelles-based solid phase extraction for the preconcentration of three polycyclic aromatic hydrocarbons (PAHs) from environmental samples [13]. However, the IL was physically adsorbed on the surface of the magnetic nanoparticles, which limited the reusability of the IL-modified magnetic materials. ILs, which are covalently bonded to supporting materials, can provide high stability and minimize IL loss during extraction and elution.

Some of developments and applications examples of PILs have already been demonstrated, such as coating in SPME, polymeric electrolytes, catalysis, etc. PIL-based SPME coatings exhibited high thermal stability and extraction selectivity, good durability and long lifetime [14], [15]. The use of poly (1-vinyl-3-butylimidazolium) bromide enabled

the fabrication of mechanically stable graphene-containing polyelectrolyte membranes [16]. Polymers anchored onto the magnetic support surface could offer the advantage of thelarge surface area and abundant adsorption sites. It was reported that magnetic materials coated with PIL proved to be a more efficient catalyst compared to the immobilization of conventional IL [17].

The present review covers ionic liquids and polymeric ionic liquids that have been used as sorptive materials in magnetic solid phase extraction MSPE and Solid phase micro-extraction (SPME), Approaches as sorbents in SPE, and highlight the recent advancements in IL-MSPE and SPME. A number of selected studies are then given introducing some of developments and applications of ILs and PILs in MSPE and SPME in order to illustrate their benefits and limitations.

2. Important Ionic Liquids

Ionic liquids which are liquids at/or below room temperature are called as room temperature ionic liquid (RTIL). Ionic liquids are self-dissociated and do not need a solvent to dissociate into cations and anions which uniquely distinguish it from classical salts like NaCl, KBr, etc, which requires a molecular solvent to dissociate into cations and anions. In general, the cations of ionic liquids are organic and large in size whereas the anions of ionic liquids are inorganic/organic entitiesof different sizes.

Most common ionic liquids are formed through the combination of (i) an organic heterocycliccationic structure of low symmetry, such as imidazolium, pyridinium, tetraalkylphosphonium, pyrrolidinum, tetraalkyammonium etc. and (ii) an inorganic or organic anion which could be polynuclear, such as Al_2Cl_7, Al_3C_{110}, hexafluorophosphate $[PF_6]$, tetrafluroborate $[BF_4]$, nitrate $[NO_3]$, octyl sulfate $[OcSO_4]$ etc [18]. It may be noted that most ionic liquids (Figure 1) have singly charged cation or anion but few years ago, ionic liquids having doubly charged species have also been reported [19].
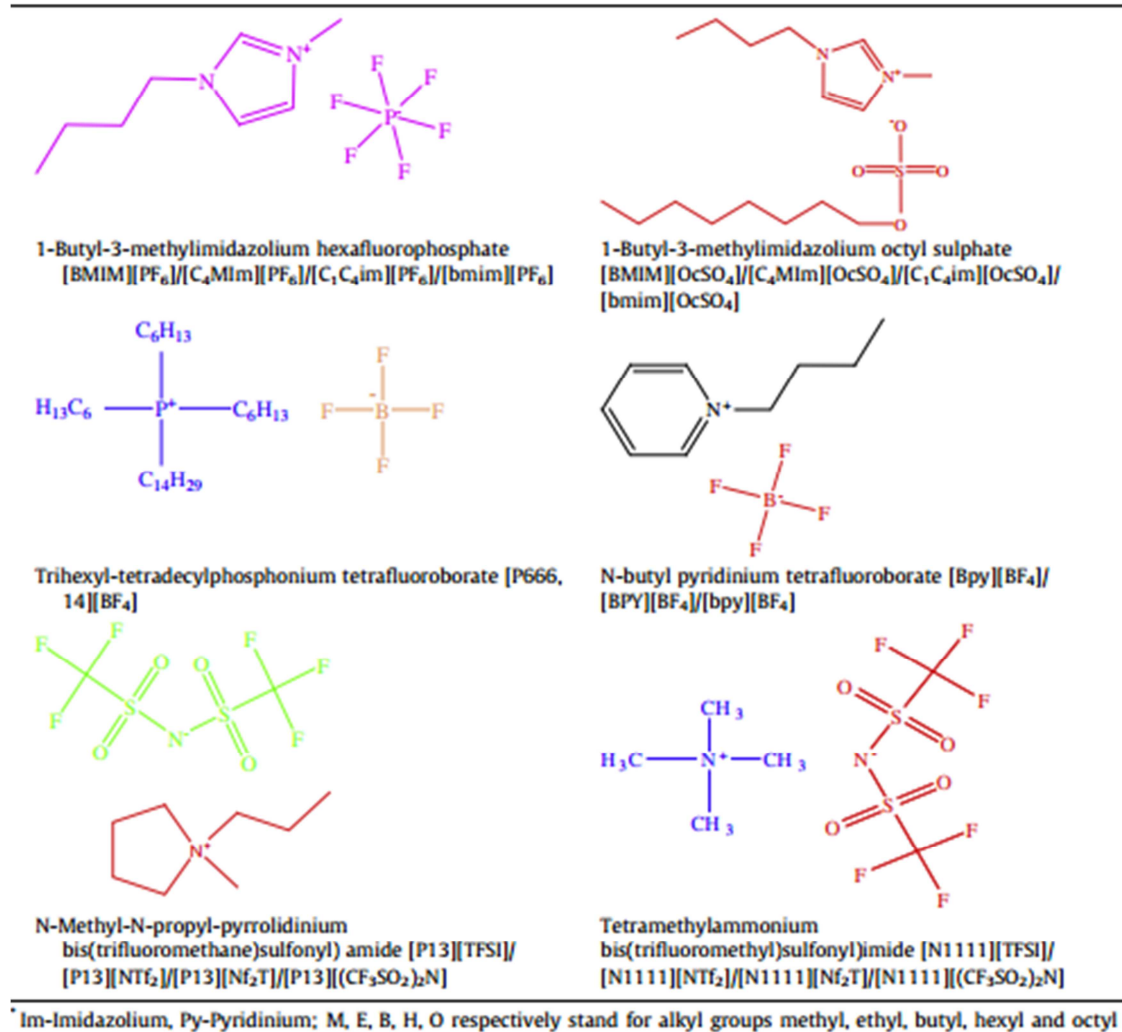

Figure 1. *Examples of some common ionic liquids with their formula structures and abbreviations.*

The unique physicochemical properties of ionic liquids make them a good replacement of standard organic solvents in a great number of different chemical reactions. Due to the chemical stability and possibility of the recycled usage, the

ionic liquids are in the field of interest of the industry [20], [21]. The properties of IL can be modified by simple changes in the nature of the cation or anion. The knowledge of the way how to change physicochemical properties of ionic liquids is crucial for their optimized design, therefore all methods used for prediction of some IL properties can be extremely useful. Theoretical chemistry offers three ways of the prediction of ionic liquid properties. Quantitative structure – property relationship (QSPR) methods are based on the extrapolation of already known or calculated properties of the training set of molecules. The newly built model of relationship can be used for the prediction of specific properties of the new molecules. Semi-empirical methods can be used to calculate the electron density (charge distribution, polarizability), molecular geometry and volume of the ion pairs [22], [23]. The high correlation between molecular volume and basic physicochemical properties of the ionic liquids was studied by Slattery et al. [24] and Wileńska et al. [25]. Empirical force field and molecular dynamics methods (MD) can be used for the prediction of physicochemical properties of ionic liquids, however, the obtained results are highly dependent on the simulation parameters.

ILs-MNPs have been applied in magnetic solid-phase extraction (MSPE) of various compounds such as flavonoids, [26], ergosterol, [27] lipase, [28] dye, [29], DNA, 19 metals, [30] phthalate esters, [31], [32] sulfonylurea herbicides [33] and enzymes. [34], [35] Some others have also studied the applications of ILs-MNPs as recyclable catalysts [36], [37].

3. Solid-Phase Extraction

Solid phase extraction (SPE) belongs to the group of sorptive-based extraction techniques, in which the sample is placed in contact with a suitable material, so the availability of different materials to carry out the extraction is essential. Research into this techniques often, therefore, focuses on developing new materials to achieve higher selectivity and capacity of the technique.

Classic sorbents used in SPE are:

(1) silica-based, modified with C18, C8, phenyl, CH, CN, or NH_2 groups;

(2) carbon-based sorbents, including graphitized carbon black (GCB) and porous graphitic carbon (PGC); and,

(3) porous polymeric sorbents, primarily the macroporous polystyrene-divinylbenzene (PS-DVB).

To improve capacity, hyper cross-linked sorbents have been developed, and, due to their ultra-high specific surface area of upto 2000 m^2/g, they provide a great number of interaction points with the analytes to be extracted. The hydrophobic structure of the original porous polymers has also been improved with the introduction of hydrophilic macroporous and hydrophilic hypercross-linked sorbents. The hydrophilicity of the sorbents can be introduced through a hydrophilic precursor monomer or by chemically modifying the PS-DVB polymer skeleton [38].

Since the late 1990s, several studies have been published to demonstrate the potential of ILs in analytical chemistry. Some of these publications are reviews of the state of the art [39] while others provide specific applications, mainly focused on stationary phases in separation techniques {e.g. gas chromatography (GC), liquid chromatography (LC) and capillary electro chromatography (CEC) [40], and as solvents or modifiers in liquid extraction techniques {e.g., liquid-liquid extraction (LLE), liquid-phase microextraction (LPME), single-drop microextraction (SDME), and solid-phase micro-extraction (SPME)[41], or as part of sorptive material in extraction techniques {e.g., SPME [42] or SPE [43]}, interest in which has been increasing lately. We should highlight that the liquid state of ILs is lost when immobilized onto a solid support. Nevertheless, under these conditions, multi-modal type interactions can be still exploited.

Magnetic Solid-Phase Extraction (MSPE)

MSPE based on the use of magnetic adsorbents, has recently attracted a great deal of attention as a new sample preparation technique [44], [45]. In some procedures magnetic adsorbents are dispersed into the sample solution, providing a fast and efficient approach to extract and enrich the target analytes. The ionic liquids that are directly used for target analytes extraction can cause not only changes in analytes conformation, but also loss of activity and can be difficult to recycle and reuse.

To solve this problem, ionic liquid modified on the surface of the magnetic nanoparticles (ILs-MNPs), which consist of bulky organic cations combining with inorganic or organic anions, has recently been developed as a new sorbent material.

The magnetic materials with captured analytes can be readily separated from sample matrix by an external magnetic field. Compared with traditional solid-phase extraction (SPE), this technique does not require column-packing, which can simplify the total operation process. Due to these unique characteristics, MSPE has found widespread applications in many fields such as food analysis, environmental analysis and biological analysis [46], [47].

4. Approaches for Solid Phase Extraction

From the methodological standpoint, two basic approaches can be recognized in SPE, on-line and off-line procedures. In off-line preconcentration/separation mode, the enriched phase is manually transferred to the detector. The on-line approach enables high sample throughput with lower sample contamination as all operations are carried out automatically.

4.1. Off-Line Mode

In the classical SPE, an appropriate sorbent is packed in a column, followed by loading the liquid sample to retain an analyte and then elution step is performed. Modern trends in SPE, except the development of novel sorptive materials, are toward simplification, miniaturization and low consumption of organic solvents and samples [48]. Stir bare sorptive extraction (SBSE) has an extraction mechanism similar to that of solid phase micro-extraction (SPME), but uses much larger extraction volume, resulting in higher absorption capacity, higher recoveries and solvent-free nature [49]. Several studies

aimed at elaborating either novel materials used for coating magnetic stirrers or new variants of SBSE are continuously being conducted, which were summarized in the recent reviews [50].

According to the extraction Conditions, different amounts of the IL-MNPs were added into the analytes solutions, which were shaken at 200 rpm for a predefined time and temperature. After extraction, the solid phase that contained the adsorbed analytes on the surface of ILs-MNPs was magnetically separated. The amounts of analytes adsorbed on the magnetic nanoadsorbents were estimated from the concentration change of analytes in solution after adsorption by different types of instruments.

Several nanomaterials have been investigated as solid phase sorbents for this technique, such as carbon nanotubes, graphene oxide and molecularly imprinted nanoparticles [51], [52]. Particularly, nanoparticles contain magnetic components allow convenient and highly efficient enrichment. Nanoparticles are dispersed into the sample solution, and after adsorption process, they are easily separated from the matrix by applying an external magnet while the solution is discarded. Then, the target analytes are desorbed with a suitable solution and nanoparticles are regenerated for reusing as it is shown schematically in Figure 2.
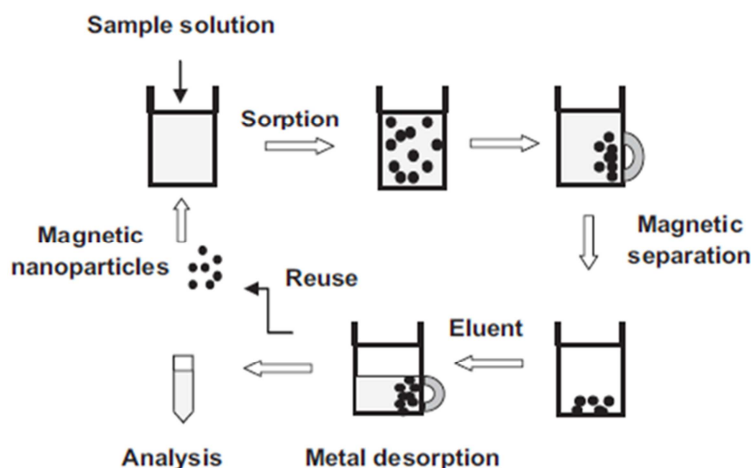

Figure 2. Schematic description of magnetic solid phase extraction.

4.2. On-Line Mode

Flow systems, where the aqueous sample is introduced into the analytical path and processed inside it under reproducible conditions, have proved to be excellent tools for the automation of sample pretreatment with on-line separation and/or preconcentration techniques based on sorption principles. Briefly, flow injection analysis (FIA) is based on an injection of a precise sample volume into a moving carrier or reagent stream. In the course of its travel through the reaction coil, the sample zone disperses and reacts with the reagent to form a detectable species [53]. As opposed to FIA, sequential injection analysis (SIA) is a fully computer controlled technique based on the use of a multi-position valve from the ports of which individual, precisely metered zones of sample and reagents are aspirated sequentially by means of the syringe pump and stacked in a holding coil [54]. Then, the segments are propelled forward towards the detector, undergoing partial mixing and hence promoting a chemical reaction, the results of which is monitored by the detector. The use of syringe pump as liquid drivers has allowed the manipulation of sample and reagent volumes at low μL levels with high precision. The third generation of flow analysis, sequential injection lab-on-valve (SI-LOB) has specific advantages and allows novel, unique applications, particularly for online separation and preconcentration of trace metals [55].

Using this approach, the contents of the SPE columns are withdrawn on-line and replaced for each analytical run, thus preventing the partial loss of their sorption capabilities and reducing the risk of contamination.

5. Some Developments and Applications of ILs/PIL in SPE and MSPE

5.1. Developments and Application of ILs in SPE and MSPE

Ionic liquids coated MNPs were used as adsorbent in solid phase extraction for separation of many analytes introduced in different studies as follow:

In the first study, the magnetic nanoparticles ($Fe_3O_4@SiO_2@IL$) were prepared via self-assembly and used as MSPE agents, combining the advantages of the ILs and the magnetic nanoparticles (MNPs). Compared with previous reports [56], the MSPE method reported herein provided a rapid and efficient sample preparation process, which enabled the treatment of a large volume of samples in a short period of time. A novel MSPE method coupled with HPLC was therefore established for the separation/analysis of RhB in food samples.

In the another work, magnetic solid phase extraction agents, $Fe_3O_4@SiO_2@ILs$ were prepared through self-assembly. This adsorbent combines the advantages of the ILs and the magnetic nanoparticles (MNPs). Compared with the previously reported works [57], this adsorbent based

MSPE provides a rapid and efficient sample preparation process, which enables the treatment of large volume samples in a short period of time. The $Fe_3O_4@SiO_2$ NPs could be used repeatedly for 10 times. Compared with other Refs. [58], reusability of the $Fe_3O_4@SiO_2$ NPs was better. Furthermore, a new method of magnetic solid phase extraction coupled with UV spectrometry for separation/analysis of linuron from real samples was established.

We should highlight that the liquid state of ILs is lost when immobilized onto a solid support. Nevertheless, under these conditions, multi-modal type interactions can be still exploited.

In the different work, researchers developed a new SPME fiber through the preparation of IL-mediated PDMS coatings chemically bonded to the carbon nanotubes. During the sol–gel process, the prepared ionic liquid-mediated sol–gel enhanced with CNTs' became chemically bonded to the fused-silica fiber with inherently effective chemical immobilization, thermal stability and higher extraction efficiency. The developed coating was then used for the determination of PAH compounds in the urine samples with GC-FID [59].

In a different article, an ultra-light weight ionic liquid-immobilized expanded perlite (IL-EP) was synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The IL-EP-SPE followed by fluorescence spectroscopy was applied to separate/analyze BPA in real food samples with reasonable results.

The potential application of the MSPE with [OMIM] PF6 ionic liquid-coated $Fe_3O_4@SiO_2$ as an adsorbent ($Fe_3O_4@SiO_2@ILs$) to extract BPA in plastic tableware was investigated in the another work. The results revealed that the $Fe_3O_4@SiO_2@ILs$ exhibited excellent adsorption properties. The method of magnetic solid phase extraction coupled with high performance liquid chromatography–fluorescence detection (HPLC-FLD) for separation/analysis of BPA from real samples was established [60].

In another work, a novel MSPE method based on magnetic NPs and mixed hemimicelles of RTILs for the preconcentration of three flavonoids (quercetin, luteolin and kaempferol) in urine samples was established. Mixed hemimicelles were prepared by adsorbing C16mimBr on the surface of $Fe_3O_4@SiO_2$ NPs and predominant experimental factors affecting the extraction efficiency were studied. To the best of our knowledge, it was the first report of using ionic liquid-coated $Fe_3O_4@SiO_2$ NPs for preconcentration of organic compounds from complex biological samples [61].

In different article, researchers have prepared a novel nano-adsorbent, Fe_3O_4@ionic liquid @methyl orange nanoparticles ($Fe_3O_4@IL@MO$ NPs) through self-assembly. This new type of nano-adsorbent combines the advantages of the IL, MO and the MNPs for separation of PAHs. Compared with the previously reported works [62], [63], this nano-adsorbent based MSPE provides a facile, rapid, and efficient sample preparation process, which enables the treatment of large volume samples in a short period of time [64].

In different work, an ionic liquid was synthesized and loaded on to the ionic liquid-β-cyclodextrin cross-linked polymer. Fourier transform infrared spectroscopy (FT-IR) was used to study the inclusion interactions of the ionic liquid-β-cyclodextrin cross-linked polymer and rhodamine B. The ionic liquid-β-cyclodextrin cross-linked polymer -solid phase extraction technique was followed by HPLC analysis for the determination of rhodamine B in real samples [65].

In different work, ILs-β-CDCP was synthesized as a solid-phase extraction material to pre-concentrate/separate magnolol coupled with HPLC for the analysis of magnolol. Compared with β-CDCP, ILs-β-CDCP showed a better adsorption capacity. The proposed method for the analysis of magnolol was satisfactory [66].

In a different article, the use of Fe_3O_4/graphene oxide functionalized MNPs has been applied for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples. According to the literature, several MNPs with different coatings such as graphene [67], carbon [68], polymers [69], bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid [70] or octadecyl groups have been already proposed to solve the same analytical problem.

In the different report, ionic liquids were used as a carrier in ferrofluid-based dispersive solid phase extraction (ILs-FFDSP). To the best of our knowledge, there is no report on the use of ionic liquid as a carrier in FF-DSPE for the separation and preconcentration of inorganic or organic species. This method is simple, rapid, and efficient for the extraction and preconcentration of CuII in water samples) from various samples. Further, in comparison with solid phase extraction, it is much faster since the extractant (sorbent) is highly dispersed in the aqueous phase. The parameters affecting extraction efficiency were studied and optimized [71].

In a different work, the imidazolium ionic liquids modified styrene-type macroporous resins were used as SILs adsorbents for SPE of BPA. A simple method for the determination of trace bisphenol A was established by coupling SILs solid-phase extraction to β-cyclodextrin modified ionic liquid carbon paste electrode (β-CD/ILCPE)-based electrochemical detection (SILs-SPE-ED) [72].

In another work, the determination of Allura Red in food by Ionic liquid β-CDCP-HPLC was done. The purpose of this work is to expand earlier work, and demonstrate the use of ionic liquid solid-phase extractants with β-cyclodextrin for the preconcentration and determination of Allura red in food [73].

In different article, an inexpensive plastic syringe was used as a simple and cost effective SPME device. In order to enhance the amount of coated material, etched fused-silica capillaries were employed for the ionic liquid coating. For comparison of the extraction efficiencies, both a Nafion membrane precoated fused-silica capillary and an untreated fused-silica capillary coated with the ionic liquid were used to extract polycyclic aromatic hydrocarbons (PAHs), which served as model compounds. To determine the stability and

the usefulness in a complex matrix, the established method was also applied for the analysis of PAHs released from the burning of mosquito coil incense [74]. Table 1. Summarized a number of selected studies were then given introducing some of the developments and applications.

Table 1. Some developments and applications of ILs in SPE and MSPE.

Adsorbent Material	Target Analyte	Extraction/Instrumental method	Sample analyzed
$Fe_3O_4@SiO_2@IL$	RhB	MSPE-HPLC	food
$Fe_3O_4@SiO_2$ NPs	linuron	SPME-UV	water
IL-PDMS	PAHs	GC-FID	urine
IL-EP	BPA	IL-EP-SPE-FS	food
$Fe_3O_4@SiO_2@IL$	BPA	HPLC	plastic
RTILs-$Fe_3O_4@SiO_2$ NPs	flavonoids	MSPE	urine
$Fe_3O_4@$ IL@ MO NPs	PAHs	MSPE	urine
IL-β-CDCP	RhB	SPE-HPLC	food
IL-β-CDCP	magnolol	SPE-HPLC	drug
$Fe_3O_4@GO$	PAHs	MSPE/GC/MS	water
IL-FF-DSP	CuII	FF-DSPE	food
β-CD/IL- CPE	bisphenol A	SILs-SPE-ED	water
IL-β-CDCP	Allura red	β-CDCP -HPLC	food
IL-FSC	PAHs	MSPE	mosquito coil incense

5.2. Developments and of PILs in SPE and MSPE

Many studies aimed to exploit the hydrogen bond accepting property of the chloride anion so as to extract polar analytes including phenols, volatile fatty acids (VFAs), and alcohols. For comparison purposes, a PIL containing the same cation but paired with bis [(trifluoromethyl) sulfonyl] imide anion, known to possess significantly low hydrogen bond basicity, was also used to extract the same analytes. In addition to performing the extraction in an aqueous matrix, heptane was also employed as the extraction solvent to investigate the selectivity of the PIL coatings towards different analytes using headspace extraction [75].

In another manuscript, researchers report a series of nine cross-linked PIL-based SPME sorbent coatings designed to increase the extraction efficiency of acrylamide. The structure of the IL monomer was tailored by introducing different functional groups to the cation and the nature of the cross-linker was designed both by modifying the structure of the cation and/or combining it with different counteranions. The extraction efficiency of the new PIL coatings towards acrylamide was investigated and compared to the previously reported studies that used PIL as acoated sorbent. The matrix-compatibility of the PIL-based fibers with complex real-world samples was also proven by quantifying acrylamide in brewed coffee and coffee powder [76].

In another manuscript, three thiophene functionalized ILs were synthesized. The electro-polymerization method was applied for the preparation of conducting polymeric ionic liquid (CPIL)-based thin films onto macro- and microelectrode substrates. These new CPILswere then investigated for the selective extraction of analytes for electrochemical preconcentration and as headspace magnetic solid phase extraction (HS-SPME) sorbent coatings in which they demonstrated high thermal stability and fiber-to-fiber reproducibility [77].

In another work, researchers reports a novel magnetic adsorbent modified with PIL, where the adsorbent provided high extraction efficiency and enrichment factors for the extraction of organophosphorus pesticides (OPPs). The developed PIL-MSPE was applied to extract four OPPs from tea drinks while high-performance liquid chromatography (HPLC) was utilized for separation and quantification. The preparation and characterization of novel adsorbent were described in detail and factors affecting the MSPE efficiency were optimized [78].

In another paper, PIL-based sorbent coatings were used for the determination of CO_2 using SPME. The structures of these PILs, namely, poly (1-vinyl-3-hexylimidazolium) bis [(trifluoromethyl)- sulfonyl] imide [poly (VHIM-NTf2)] and poly (1-vinyl-3-hexylimidazolium) taurate [poly (VHIM-taurate)], were carefully tailored to enhance CO_2 solubility. SPME fibers were coated with neat PILs as well as mixtures with desired weight percentage of these two PILs. For comparison, two commercially available SPME fibers, namely, poly (dimethylsiloxane) (PDMS) (film thickness of 7 μm) and Carboxen-PDMS (film thickness of 75 μm), were included in this study. The sensitivity, linearity and linear range of these sorbent coatings were determined from calibration curves generated in pure CO_2 and CO_2 spiked with a known amount of air. The storage capability under different storage conditions was examined for selected fibers, revealing that PIL-based sorbent coatings provided superior abilities in retaining CO_2 compared to the commercial carboxen fiber. Table 2. showed a number of selected studies were then given introducing some of the developments and applications.

Table 2. Some developments and applications of PILs in SPE and MSPE.

Adsorbent Material	Analyte	Extraction/Instrumental method	Sample analyzed
PIL Based fiber	acryl amide	SPME	coffee
CPIL	polar analytes	HS-SPME	polar compounds
MPIL	OPPs	MSPE-HPLC	tea drinks
PIL- fiber coated	CO_2	SPME	amount of air

6. Conclusion

The developments of ionic liquid and poly ionic liquid, approaches, and applications in magnetic solid phase extraction and solid phase microextraction are already well established. Furthermore, the magnetic solid phase extraction conditions in order to enhance the selectivity and the capacity of different materials when applying them to preconcentrate complex samples was studied. Nevertheless, their selectivity and capacity may be further fine-tuned by selecting the type of adsorbent.

Once the benefits of ionic liquid and poly ionic liquid as magnetic solid phase extraction sorbents have been demonstrated, their consolidation as conventional magnetic solid phase extraction materials will envisaged in the near future and more so when they are commercialized, so scientists with an interest in mixed-mode sorbent technology may also find that these materials provide new, exciting opportunities.

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