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Sample Treatments Based on Ionic Liquids

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1. Introduction

The term ionic liquid (IL) is nowadays used to define a broad class of semi-organic salts or salt mixtures composed entirely by ions which are liquid in the range 180-600 K. They are hydrogen bonded substances with strong interionic interactions which condition their crystallographic structure. The presence of at least one constituent ion with a delocalized charge prevents the formation of a stable crystal lattice (Palacio & Bhushan, 2008).

Although ILs are known since 1914, their expansion arrives with the availability of air and moisture stable ones. This second generation of ILs combines the unique properties of the former with the ease of handling of the latter. Their most relevant attributes or properties are as follows: negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water, inorganic and organic substances, a wide electrochemical window, high conductivity, high heat capacity and suitability to control reactions.

The electronic and steric features of the cation and anion condition their physical-chemical properties. Their synthetic flexibility permits the modulation or adaptation of certain properties of the IL for a particular objective. Density, viscosity and solubility (crucial in any extraction procedure) can be cited among the more tuneable features. Moreover, the nature of cation and anion structures influences the acid/basic and solvent properties and raises the differences with conventional molecular solvents. Finally, the potential introduction of functional groups capable of having complementary interactions with other solvents or molecules opens up new variability on ILs properties and behavior.

A huge number of potential cation-anion combinations are possible, which gives rise to an unusual large number of different compounds. The most popular high weight organic cations are imidazolium, pyridinium, pyrrolidinium quaternary ammonium and tetraalkylphosphonium. The most used by far are the 1,3-dialkylimidazolium salts as the likely result of their easily tailored properties. Regarding the most preferred organic anions, perfluorated (e.g. trifluoromethanesulphonate) and halogen-free (e.g. n-alkylsulphates) are among the most reported in the literature.

The presence of impurities is a very remarkable aspect in the use of any IL, as its properties can be dramatically altered by the presence of trace amounts of compounds usually arising from unreacted starting material or water. This fact has led to irreproducibility between reactions and procedures. The overcoming of such limitation is crucial for the implementation of ILs in analytical science and their consolidation as an alternative to traditional molecular organic solvents.

2. Ionic liquids in analytical chemistry

Ionic liquids can be successfully used in different steps of the (bio)chemical measurement process. In addition to selectivity and sensitivity improvement of existing methodologies, ILs can offer to the analytical scientists original alternatives to face up new applications.

Probably, their use in the preliminary steps is of advantage as they can markedly reduce the sample pretreatment step while improving its efficiency. This section presents a current picture of the contribution of ILs to improve the analytical process. It must be taken into consideration that the following sections will be exclusively devoted to the role of ionic liquids in sample preparation.

2.1 Extraction

Ionic liquids have been extensively used for the liquid-liquid extraction of metals (aided by complexation reagent), small organic molecules (hydrocarbons, PAHs) and also large biomolecules such as proteins and DNA thanks to hydrophobic interactions helped by electrostatic and also salting out effects. This wide applicability derives from the possibility of ad hoc design of ionic liquid used as extractant. In this way, the selectivity and efficiency can be modulated from the specific application as well as the solubility and miscibility between the extractant and the sample matrix. Several studies can be found in the literature dealing with this topic. For example, it has been established that the distribution coefficients for different metal cations were maximum for shorter 1-alkyl-3-methyl imidazolium ILs (C_4 expected). On the contrary, the extraction of proteins is favored with the use of ILs presenting a long alkyl chain in the cation. Particularly interesting is the applicability of ionic liquids to break a variety of azeotropic systems and chiral separations.

Liquid-liquid extraction has been moved to the miniaturized version of the technique in order to overcome its negative connotations. As expected, ILs have played a crucial role in the development of several modalities of liquid phase microextraction (LPME). 1-octyl-3-methylimidazolium- PF_6 demonstrated excellent performance for the extraction of PAHs from waters in both, direct immersion and headspace LPME. Since then, ILs have been used in dynamic LPME, hollow fiber protected LPME, single drop microextraction and dispersive liquid-liquid microextraction.

The applicability of ILs in solid-phase microextraction (SPME) was established by Liu *et al.* (Liu *et al.*, 2005) for the determination of benzene, toluene, ethylbenzene and xylene in paints. The thermal stability, extraction capacity and the easy immobilization on fused silica capillaries are among the most remarkable advantages of this coating. Their usefulness has been demonstrated in both headspace and direct immersion approach.

All these extraction modalities will be deeply commented in section 4.

2.2 Chromatography

Room temperature ionic liquids have been used as novel stationary phases in a variety of chromatographic separations. The research in gas chromatographic uses of ILs has been leaded by Armstrong's group, who studied the behavior of $[C_4MIM][PF_6]$ and $[C_4MIM][Cl]$ as coatings in fused silica capillary columns (Armstrong *et al.*, 1999). The most valuable features in this application field are the high viscosity and thermal stability together with the easy immobilization on the inner surface of the fused silica capillary. The versatile combinations of ILs permit the efficient separation of polar and non-polar compounds, although long retention times and tailing peaks can be obtained for alcohols and organic

acids and even irreversible interaction of alkylamines has been reported. Notwithstanding this, the design of specific ionic liquids can overcome this limitation (Anderson & Armstrong, 2003).

In liquid chromatography, ILs can be used either as mobile phase modifiers or as stationary phases. The high viscosity and UV absorption of ILs limits their use as mobile phases. However, their presence at low concentrations (as additives) results in a decreased peak tailing, reduced band broadening and thus improved resolution. This effect is justified by a competitive reaction between imidazolium cations and the polar groups of the analytes for the silanol groups of the silica surface. Additional hydrophobic interactions between the alkyl chain of the cation and the C₁₈ groups can also be behind this favorable effect of the ionic additive. More recently, ionic liquid-based stationary phases with immobilized imidazolium based ILs have been synthesized. In most cases, they work under strong anion exchange character and reversed phase interactions.

2.3 Electrophoresis

Ionic liquids have been employed to improve the electrophoretic separation in non aqueous capillary electrophoresis as their use in the conventional mode is hindered by their high viscosity and conductivity. ILs have been used to separate water-insoluble dyes due to the modification of the overall electrophoretic mobility of the system and the dissociation of the analytes in presence of the ILs. Further research has demonstrated the capability of ILs to improve the electrophoretic separation of chiral and achiral compounds aided by polymeric surfactants (Mwongela *et al.*, 2003).

Ionic liquids have also been covalently bonded to the inner surface of the fused silica capillary to reduce the analytes adsorption and reverse the electrosmotic flow (Qin & Li, 2002). Biomolecules (DNA and basic proteins), drugs, inorganic cations and alkylphosphonic acids have been successfully separated using capillaries modified with ILs. The reusability of the capillary (up to 96 runs) and the reproducibility improvement have been reported as additional advantages of this modality.

2.4 Sensors

The applicability of ionic liquids in electrochemistry has been boosted by the high ionic conductivity, low volatility and good redox robustness. However, most of the references deal with the electrodes construction and voltammetric data generation, being the analytical applications very limited yet. The high viscosity of ILs has been exploited for the development of membrane-free electrode modified with a thin layer of IL (Buzzeo *et al.*, 2004). They would be especially useful under extreme temperature conditions owing to their thermal stability and low volatility. The combination of hydrophobic ionic liquids, such as 1-ethyl-3-methylimidazolium trifluoromethylsulfonate, with membranes (e.g. Nafion) has been proposed as alternative to water for the construction of electromechanical actuators and sensors (Bennett & Leo, 2004). Although they are more stable operating in air, their response is rather slow in comparison with the use of water as consequence of the higher viscosity of the medium. Moreover, irreversible redox reactions can also occur.

More relevant is the use of ionic liquids in sensing approaches for the determination of organic vapors and gases. In this regard, variation on the viscosity of ionic liquids has been successfully employed as sensing material for the fabrication of quartz crystal microbalances (Liang *et al.*, 2002).

3. Ionic liquids as solvents

The solvent power of ILs, recently reviewed (Poole & Poole, 2010), has attracted much attention not only for extraction but also for the use of ILs as solvents in synthesis. The use of ILs as solvents is based on their peculiar physical and solvation properties. Among physical characteristics, we can highlight their high density, viscosity and conductivity, their low vapor pressure, and their miscibility with other organic solvents and water. ILs involve a great variety of compounds, in the range of 10^4 (Chiappe & Pieraccini, 2005), which clearly indicates their versatility. Moreover, some of their characteristics are tunable and therefore task-specific ILs (Davis, 2004) can be synthesized for a defined application. The environmental friendly nature of ILs, which is under scrutiny (Couling *et al.*, 2006), is also a positive aspect. In fact their recycling is easier compared to conventional organic solvents due to their special physical properties.

ILs have been extensively used in liquid-liquid extraction (LLE) for the isolation from aqueous samples of a great variety of compounds. In this sense, they have been selected for the extraction of metals following three different procedures (Zhao *et al.*, 2005):

- Extraction of metals by using crown ethers. The resulted crown- ether complexes present a high hydrophobicity but they still remain a residual electric charge. The use of ILs for extraction of these complexes presents efficiencies up to 10^4 better compared to conventional organic solvents (Dai *et al.* 1999).
- Extraction of metals as neutral complexes using anionic ligands (Wei *et al.*, 2003) (Hirayama *et al.* 2005). This approach has been extensively used for the extraction of different metals such as mercury (Li *et al.*, 2007a), aluminium (Li *et al.* 2007b) or nickel (Dadfarnia *et al.*, 2010).
- Extraction of metals using task-specific ILs which present a cationic interchangeable group in their structure (Visser *et al.*, 2001).

The chemical nature of ILs (tunable polarity and miscibility with water) allows also their use for the extraction of organic compounds from water (Simone *et al.*, 2010).

In summary, ILs have become an important tool in sample preparation, especially in microextraction techniques. Their peculiar characteristics have allowed the improvement of the existing techniques and moreover the development of new ones. These aspects will be considered in depth in the following section of the chapter.

4. Ionic liquids in microextraction techniques

Sample pre-treatment is a key step in the analytical process in order to improve the sensitivity (by the preconcentration of the target analytes) and selectivity (by avoiding the presence of potential interferences) as well as to overcome the incompatibility with the detection system. The ideal sample treatment should be: a) simple, reducing the number of steps; b) automatic, reducing operator manipulation; c) suitable for miniaturization, reducing sample and solvent consumption; d) rapid, to allow a high sample throughput in order to resolve problems in real time; e) inexpensive; and f) safe to the operators and environment (Lucena *et al.* 2009).

Microextraction techniques, including solid phase microextraction (SPME) and liquid phase microextraction (LPME), emerged in the 1990's as a consequence of analytical chemistry evolution towards automation, miniaturization and simplification. In this context, the unusual physical properties of ionic liquids as well as their excellent solvent properties have been exploited in a large extent.

4.1 Ionic liquid in liquid phase microextraction

Liquid-liquid extraction (LLE), a classical sample treatment technique, is based on the partitioning (distribution) of a chemical substance between two immiscible phases. In the usual approach the aqueous sample containing the analytes is mixed with an appropriate organic solvent which presents a chemical affinity towards the target analyte at the operating conditions (temperature, pH, ionic strength ...etc). After a vigorous shaken both phases are conveniently mixed, the transference of the analytes from the donor to the acceptor phase taking place. Despite the different approaches developed, LLE remains as a manual technique involving different steps (subsequent extractions, back-extractions, evaporation of the extracts ...etc) which are a source of potential contamination or analyte losses, directly affecting the reproducibility of the final measurements. Moreover, the technique is tedious, time consuming and it requires the use of large volumes of pure organic solvents which are expensive and hazardous to operators and environment.

In this scenario, LPME emerged as an alternative to classical LLE. Dasgupta (Liu & Dasgupta, 1996) proposed in 1996 for the very first time the use of solvents in the low microliter range as extractants in LLE. Apart from the obvious economical and safety connotations, the reduction of the volume of extractant has allowed an evident improvement in the enrichment factors since the sample/extractant volumes ratio is dramatically increased.

From this origin, LPME has evolved spectacularly and it has become a reality in routine laboratories. In this sense, a large number of sub-techniques have been developed in order to solve different analytical problems. Taking into account that this chapter is focused on the role of ILs in this context, only those techniques which make use of the peculiar characteristic of ILs will be considered in depth.

4.1.1 Ionic liquids in single drop microextraction

Single drop microextraction technique (SDME) was firstly proposed by Jeannot and Cantwell in 1996 (Jeannot & Cantwell, 1996). Despite the utility of this contribution, the widespread use of SDME is due basically to the works published in 1997, almost simultaneously, by Jeannot and Cantwell (Jeannot & Cantwell, 1997) and He and Lee (He & Lee, 1997). In these articles, the authors proposed the use of a conventional microsyringe as extraction manifold for SDME. Theoretically, SDME is based on the transference by passive diffusion of the analytes from the sample to a micro-drop of extractant which is located in the tip of a microsyringe. The technique involves in the same step the isolation and preconcentration of the target analytes allowing also the direct injection of the extracts in the analytical instrument. Depending on the phases involved, two different extractions schemes are possible. In the direct immersion mode (DI-SDME), the microsyringe tip is inserted into the aqueous phase and the drop is directly exposed to the sample. In the headspace mode (HS-SDME) the extractant is exposed to the vapor phase generated from the sample, the extraction involving three different phases (aqueous, headspace and organic extractant).

In both modes, conventional organic solvents have been successfully applied for the resolution of diverse analytical problems. However, ILs present special characteristics like tunable polarity and miscibility with water as well as exceptional physical (viscosity, surface tension...) and chemical (extraction capabilities) properties which make them so attractive as alternatives to conventional solvents. Moreover, ILs have been considered as green solvents due to their negligible vapor pressure compared with volatile organic solvents, making them an interesting tool with respect to the safety to operators and environment.

Liu *et al.* (Liu *et al.*, 2003) proposed for the first time the use of ILs in SDME (in both extraction modes) for the extraction of polycyclic aromatic hydrocarbons from water samples. The IL employed, 1-octyl-3-methyl imidazolium hexafluorophosphate, ([C₈MIM][PF₆]), presented superior capabilities compared to 1-octanol in terms of enrichment factors. On the one hand, the adequate viscosity and surface tension of ILs allow the suspension of larger drops in the tip of the microsyringe. On the other hand, their negligible vapor pressure makes the microdrop more stable (avoiding potential evaporation during the extraction) in the headspace mode.

DI-SDME is the preferred technique for the isolation of non-volatile and/or thermolabile compounds from aqueous samples. The solvents employed in these procedures should fulfil some requirements like immiscibility with water (in order to avoid extractant losses), affinity towards the analytes (to achieve good preconcentration factors) and good stability on the microsyringe tip. 1-alkyl-3-methyl imidazolium hexafluorophosphate ([C_nMIM][PF₆] with n=4,6,8) ILs have been extensively used in DI-SDME for the extraction of organic compounds as well as inorganic species. Vidal *et al.* have proposed the use of [C₆MIM][PF₆] for the extraction of typical UV-filters in water samples (Vidal *et al.*, 2007a) (Vidal *et al.* 2010). The chemical compatibility of these ILs with the chromatographic columns allows the separation and determination of the extracted analytes by liquid chromatography coupled to UV detection. Preconcentration factors up to 98 (for 3-benzophenone) were obtained. In these articles, the authors present an interesting study of the influence of different chemical variables on the extraction of a given analyte.

In the same way, ILs have been employed for the extraction of inorganic species such as mercury, manganese or lead. According to their ionic nature, these analytes cannot be directly isolated in the ILs phase, a previous complexation with an appropriate ligand being necessary. Pena-Pereira *et al.* used [C₆MIM][PF₆] for the extraction of mercury species, including inorganic and organic ones, making speciation possible by HPLC-UV (Pena-Pereira *et al.*, 2009). In other sense, for the total determination of metals electrothermal atomic absorption spectrometry (ETAAS) is preferred due to its selectivity and sensitivity levels. Manzoori *et al.* proposed for the first time the direct coupling of DI-SDME using ILs with ETAAS (Manzoori *et al.*, 2009a). This coupling, which is possible due to an adequate selection of the pyrolysis temperature and time, allows the determination of manganese in the low part per billion range using [C₄MIM][PF₆] as extractant. The same procedure has been proposed for the determination of lead in water and food samples with similar success (Manzoori *et al.*, 2009b). Although the use of [C_nMIM][PF₆] ILs is predominant, Martinis *et al.* have proposed the use of tetradecyl(trihexyl)phosphonium chloride as extractant for the determination of lead in waters (Martinis *et al.*, 2010).

DI-SDME effectiveness is restricted by the stability of the drop in the microsyringe tip, which limits the stirring of the sample solution and involves the use of drops into the 2-10 µL range. Different approaches have been developed in order to overcome these limitations. Cycle flow configuration (Xia *et al.* 2005) allows the free flowing of the sample through the IL microdrop avoiding its potential detaching during the extraction. This approach has allowed the determination of cobalt, mercury and lead in biological and environmental samples by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) (Xia *et al.*, 2008). In other sense, dynamic liquid-phase microextraction has become an excellent alternative when higher volumes of ILs (in the range of 50 µL) are required for liquid chromatographic analysis (Cruz- Vera *et al.* 2008). This approach makes use of a special manifold, completely mechanized, which performs all the steps involved in

the extraction. The obtained enrichment factors, in the range from 10 to 20, are acceptable for the resolution of different analytical problems such as the determination of non steroidal anti-inflammatory drugs or phenothiazines derivatives in biological samples (Cruz-Vera *et al.* 2009a). In samples of biological concern, ILs seem to present an excellent selectivity towards the target analytes, clean extracts being obtained after sample pretreatment.

The non-volatility of ILs, due to their low vapor pressure, makes them superior solvents than the conventional organic ones in HS-SDME. In fact, the evaporation of the solvent during the extraction is a critical limitation since it affects the extraction effectiveness and reproducibility. Therefore, ILs have been extensively used in this context for the determination in environmental samples of several contaminants such as chlorinated anilines (Peng *et al.*, 2005), organochlorine pesticides (Ye *et al.*, 2006), phenols (Ye *et al.* 2007), chlorobenzenes (Vidal *et al.*, 2007b) and aromatic amines (Zhou & Ye, 2008). Although HS-SDME is usually performed in conventional furnaces or heating baths, the use of microwave energy can be employed improving the expeditiousness of the extractions (Vidal *et al.*, 2007c). Moreover, in the latter approach the design allows the heating of the sample while the ILs remains unheated, which clearly improves the efficiency of the extraction.

All the above described analytical methods use liquid chromatography or atomic techniques for the determination of the extracted analytes, even when volatile compounds are under study. This fact is ascribed to the non-volatility of ILs which is a clear limitation in gas chromatography (GC). In fact, the presence of ILs dirties the chromatograph and even blocks the analytical column making the analysis unfeasible. Some research groups have focused their efforts in the development of interfaces and/or strategies that overcomes this shortcoming making possible the use of IL in GC. The first approach, which was proposed in 2008, made use of a special removable interface directly coupled to the chromatograph which allowed analytes desorption from the ILs avoiding the entering of the solvent in the system (Aguilera-Herrador *et al.*, 2008a). The excellent performance of the interface has been exploited in some applications which use ILs in HS-SDME for the determination of monoaromatic hydrocarbons (Aguilera-Herrador *et al.*, 2008b) and halogenated hydrocarbons (Aguilera-Herrador *et al.*, 2008c) in waters. The versatility of the interface makes possible its application with other instrumental techniques such as ion-mobility spectrometry (Aguilera-Herrador *et al.*, 2009).

Zhao and co-workers proposed another alternative for making compatible the use of ILs with GC. In this case, a minimal modification of the injection liner and a special injection procedure are required (Zhao *et al.*, 2008a). The microsyringe with the IL containing the extracted analytes is inserted in the injector of the chromatograph and the microdrop is exposed to the carrier gas in the liner, which is employed as desorption chamber. Once injected the analytes in the chromatographic column, the IL is retracted into the syringe avoiding its introduction in the chromatograph. A similar approach has been recently proposed for the determination of pesticides in soil samples (Zhang & Lee, 2010). Finally, the application of a commercially available thermal desorption unit especially employed for stir bar sorptive extraction (SBSE) has been also proposed for this coupling (Chisvert *et al.* 2009). The commercial desorption unit is modified including an inner tube in order to increase the sample throughput.

In all the described applications, both in DI-SDME and HS-SDME, pure ILs are used as extractants. However, special combinations of IL with chemical modifiers can be also employed. Micellar ionic liquids, which are the result of combining ILs with surfactants, have been recently evaluated for the extraction of aromatic compounds from aqueous

samples (Yao *et al.*, 2010). The obtained results indicate the good extractability of micellar ILs as well as a special selectivity towards the evaluated analytes.

4.1.2 Ionic liquids in hollow fiber protected liquid phase microextraction

The instability of the drop in the syringe tip may cause its detachment during the extraction, which is undesirable. Hollow fiber protected liquid phase microextraction (HF-LPME) faces up this shortcoming using a polymeric cylindrical membrane as container for the extraction solvent (Pedersen-Bjergaard & Rasmussen, 1999). The extraction solvent is located in the lumen of a hollow fiber of minimal dimensions (600 μm I.D., 200 μm of wall thickness and variable porosity) usually made in polypropylene. According to the phases involved in the extraction, two different modalities are possible. In the two phases mode (2P-HF-LPME) the extraction solvent is located in the lumen of the fiber as well as in the pores. This type of extraction, which is similar to the classical LLE, is ideal for hydrophobic analytes. In the three phases mode (3P-HF-LPME) the organic solvent is located in the pores of the membrane acting as physical barrier (supported liquid membrane, SLM) between two aqueous phases, namely: the donor (sample) and the acceptor (extractant). This extraction mode, similar to classical LLE with back-extraction, is the alternative of choice for hydrophobic ionizable compounds. In fact, in 3P-HF-LPME the pH gradient established at both sides of the liquid membrane is the driving force of the extraction. Conventional organic solvents (like toluene, undecane, dihexylether and octanol) have been successfully applied in both extraction modes although their tendency to evaporation is a critical aspect being a key source of irreproducibility. Once again, ILs are a good alternative to this solvents due to their peculiar characteristics.

Fortunato *et al.* suggested the potential of $[\text{C}_n\text{MIM}]$ -based ILs as supported liquid membranes due to their high viscosities and interfacial tensions and their low solubility in water when certain types of anions are employed (Fortunato *et al.*, 2004). This usefulness has been later on demonstrated by different research groups. Peng *et al.* proposed the use of $[\text{C}_8\text{MIM}][\text{PF}_6]$ as supported liquid membrane for the extraction of chlorophenols from water samples (Peng *et al.*, 2007). The effective immobilization of the IL in the pores of the hollow fiber was demonstrated by the authors using scanning electron microscopy (SEM). The SEM pictures obtained before and after the impregnation process are presented in Figure 1. The

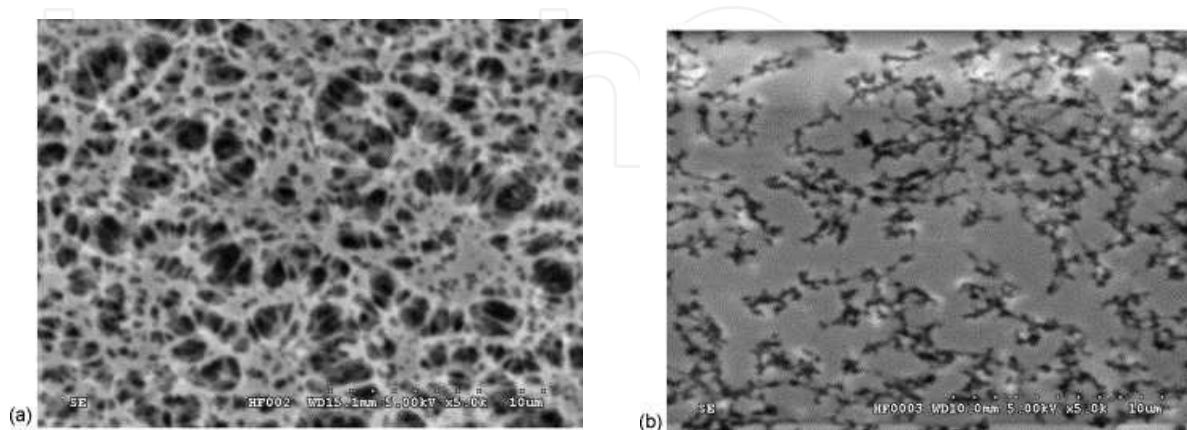


Fig. 1. Scanning electron microscopy pictures of the inner surface of a polypropylene hollow fiber (a) before and (b) after its impregnation with ionic liquid. Picture magnified by 5000 times. Figure from Peng *et al.* (2007) and reproduced with permission of Elsevier.

potential of ILs as SLM can be also ascribed to their chemical characteristics which make possible the development of special applications. On the one hand, ILs present higher polarities compared to the conventional organic solvents used as SLM. This fact has been exploited for the extraction of sulphonamides in environmental samples which are hard to extract with conventional solvents (Tao *et al.*, 2009). On the other hand, ILs present variable solubility in water and organic solvents. In this sense Basheer *et al.* proposed a special 3P-HF-LPME with the IL acting a SLM between an aqueous phase (the sample) and an organic phase (the acceptor). The method allows the determination of aliphatic and aromatic hydrocarbons in storm water by GC since the organic extracts can be directly injected in the chromatograph (Basheer *et al.*, 2008). Finally, the good performance of ILs in the 2P-HF-LPME has been recently demonstrated by the determination of lead and nickel using ETAAS (Abulhassani *et al.* 2010).

4.1.3 Ionic liquids in dispersive liquid-liquid microextraction

Microextraction techniques are surface dependent processes. Due to the small contact area between sample and extractant, the kinetic of the extraction process is too low and the time necessary to achieve the distribution equilibrium is unpractical for analysis purposes. *Dispersive liquid-liquid microextraction* (DLLME) faces up this shortcoming using an innovative approach (Rezaee *et al.*, 2006). In DLLME the extractant solvent is dispersed physically, chemically or assisted by an external energy source, in the sample in order to obtain a cloud of fine extractant drops, increasing dramatically the contact surface with the sample. DLLME allows the rapid extraction, almost instantaneously, of the analytes providing therefore excellent enrichment factors since the distribution equilibrium is achieved. In classical DLLME the extraction solvent should fulfil some general requirements such as: (a) immiscibility with water; (b) good chemical affinity towards the target analytes and (c) low vapor pressures. Moreover, taking into account that the extractant is recovered by centrifugation after the extraction, the solvent must be denser than water. In the light of these requirements, ILs are excellent solvents for DLLME.

Fan *et al.* proposed for the first time the use of ILs in DLLME for the determination of aromatic amines in water samples (Fan *et al.*, 2008). The IL, [C₄MIM][PF₆], is directly added to the sample and the mixture is aspirated in a 1mL-microsyringe and later on discharged in a test tube. The process is repeated twice producing the physical dispersion of the IL into the sample and providing a cloudy solution of fine microdrops. Enrichment factors in the range of 31 to 269 are obtained allowing the determination of the analytes in the low µg/L level. Physical dispersion has been also applied for the determination of phenols in waters (Fan *et al.*, 2009).

According to Liu and co-workers (Liu *et al.*, 2009a), chemical dispersion is more effective than physical dispersion when ILs are used for the extraction of heterocyclic insecticides in water samples. In fact, the extraction recoveries were 5 fold better when an organic solvent is employed as disperser. Chemical dispersion is based on the use of an organic solvent (called disperser), which is miscible with the sample (water) and the extractant (IL). A mixture of the disperser and extractant solvents, in the appropriate proportion, is rapidly injected into the sample forming the cloudy solution immediately. After a determined period of time (named extraction time) the resulted mixture is centrifuged in order to recover the IL containing the isolated analytes. This strategy has been employed for the determination of organophosphorus pesticides (He *et al.*, 2009a), polycyclic aromatic

hydrocarbons (Pena *et al.*, 2009) and bactericides (Zhao *et al.*, 2010a) in water samples. As well as other microextraction techniques, DLLME can be used for the extraction and determination of inorganic species in liquid samples. In order to favor the extraction, an appropriate ligand has to be added to the sample to form the corresponding chelate which is the extractable substance. Thus, the extraction of zinc (Abdolmohammad-Zadeh & Sadeghi, 2009), cobalt (Berton & Wuilloud, 2010a) and aluminium (Abdolmohammad-Zadeh & Sadeghi, 2010) have been successfully accomplished. DLLME can also operate with solid samples but a previous treatment is always required. A specific amount of sample is located in a container and the analytes are extracted by leaching with an appropriate solvent (usually acetonitrile). The extracts, which also contain matrix compounds, are later on evaporated and reconstituted in water. Once the aqueous matrix is obtained, the DLLME procedure is developed. In this way the determination of pesticides in bananas (Ravelo-Pérez *et al.*, 2009a) and table grapes and plums (Ravelo-Pérez *et al.* 2009b) by liquid chromatography have been possible. Moreover, the versatility of DLLME allows the treatment of complex samples. In fact, Wang *et al.* have determined triazines in honey. The sample (2 g) has to be conveniently diluted with 20 mL of water before the extraction. The authors proposed the use of a surfactant (Triton X 114) as disperser for the extractant ($[\text{C}_6\text{MIM}][\text{PF}_6]$). Both, disperser and extractant, are directly added to the diluted sample and the mixture is vigorously shaken for 10 min. After the extraction, the IL is recovered by centrifugation and finally analyzed by HPLC (Wang *et al.*, 2010).

The use of IL-based microextraction techniques for the treatment of samples with a high content of electrolytes is usually problematic since the solubility of a given IL in water dramatically depends on the ionic strength. At high levels of ionic strength, the IL is completely soluble in water and its recovery after the extraction is unaffordable. This phenomenon is caused essentially by an ion exchange process, the so-called metathesis reaction, between the IL and the electrolytes present in the sample. In this way, when a $[\text{C}_n\text{MIM}][\text{PF}_6]$ -based IL is introduced in a sample with a high concentration of chloride, the chloride anion may exchange with the hexafluorophosphate. As a consequence of this metathesis reaction a new IL ($[\text{C}_6\text{MIM}][\text{Cl}]$), completely soluble in water, is produced. Yousefi *et al.* have proposed a strategy in order to minimize this reaction by the external addition of NaPF_6 to the sample (Yousefi & Shemirani, 2010). Due to the common ion effect, the solubility of the IL decreases even in the presence of high concentration of electrolytes. This approach has been applied in a DLLME configuration for the determination of lead and cadmium in saline aqueous samples by FAAS. The common ion effect has also supported the development of a novel microextraction technique called *in situ solvent formation microextraction* (ISFME) (Baghdadi & Shemirani, 2009). In ISFME, a water-miscible IL (such as $[\text{C}_6\text{MIM}][\text{BF}_4]$) is added to the sample, being completely dissolved and therefore maximizing the contact surface with the target analytes. Later on, a common ion reagent (like NaPF_6) is added to the extraction vial inducing the metathesis reaction. As a consequence, a water-immiscible IL (in this case $[\text{C}_6\text{MIM}][\text{PF}_6]$) is formed which is finally recovered by centrifugation. ISFME has been characterized in depth by Yao & Anderson (Yao & Anderson, 2009). The authors have demonstrated the superior features of ISFME compared to traditionally DLLME or DI-SDME, using ($[\text{C}_4\text{MIM}][\text{Cl}]$ and LiNTf_2 as IL and common ion reagent, respectively. Enrichment factors in the range of 189 to 753 have been obtained for the determination of 13 aromatic compounds in water samples. ISFME has been also used for the determination of cadmium in saline samples by FAAS providing limits of detection of 0.07 $\mu\text{g/L}$ (Mahpishanian & Shemirani, 2010).

The dispersion of the extraction solvent into the sample is the crucial step in any DLLME and different alternatives, apart from the physical and chemical approaches, have been developed in recent years. In these novel approaches, an external energy source is employed in order to assist the dispersion process. The technique, *temperature controlled ionic liquid dispersive liquid phase microextraction* (TILDLME) was proposed in 2008 by Zhou and co-workers (Zhou *et al.*, 2008a) and it uses an external heat source. TILDLME is based on different well established steps. First of all, a specific amount of IL is added to the sample which is subsequently incubated at a high temperature (in the range of 45-90°C) for an appropriate time. During the heating of the sample, the IL is completely dispersed, even solubilized, into the sample matrix maximizing the contact area. Later on, the vial is introduced in an ice-bath decreasing the temperature of the mixture. In such conditions, the IL becomes insoluble and a cloudy solution appears in the extraction vial. After a proper extraction time, the mixture is centrifuged and the IL, with the extracted analytes, is recovered for its subsequent analysis. In TILDLME three especial properties of ILs are exploited, namely: (a) their good extractability towards a great variety of compounds; (b) their negligible vapor pressure which avoids the evaporation of the extractant during the heating process, and (c) their variable water-solubility which directly depends on the working temperature. Compared to classical DLLME, TILDLME provides better enrichment factors, especially for polar substances, since no chemical disperser is employed. Moreover, the contact area between sample and extractant is dramatically increased. TILDLME has been successfully applied for the determination of organophosphorous pesticides (Zhou *et al.*, 2008b), herbicides (Zhou *et al.*, 2009a) or bactericides (Zhao *et al.*, 2010b). As other extraction techniques previously described, TILDLME can be also employed for the extraction of inorganic species such as vanadium (Berton *et al.*, 2009) or lead (Bai *et al.*, 2010). In 2008, the *cold induced aggregation microextraction* (CIAM) technique is introduced for the first time (Baghdadi & Sheminari, 2008). CIAM is similar to TILDLME but lower temperatures are used in the incubation step. CIAM has been successfully used for the determination of cobalt in water samples (Gharehbaghi *et al.*, 2009).

Ultrasounds can also be used to assist DLLME originating a new technique which is called *ultrasound-assisted ionic liquid dispersive liquid-liquid phase microextraction* (USA-DLLME) (Zhou *et al.*, 2009b). In USA-DLLME the IL is dispersed by using an ultrasound source and once the IL is dispersed, the extraction vessel is introduced in an ice-bath inducing the aggregation of the IL. The resultant cloudy solution is finally centrifuged and the IL, with the extracted analytes, is recovered for its subsequent analysis. Conventional or high energy ultrasounds (Mao *et al.*, 2009) can be employed. As the previously described techniques, the versatility of USA-DLLME allows its application for the resolution of diverse analytical problems. In this sense, it has been used for the extraction of cadmium from water samples (Li *et al.*, 2009).

In the light of the results, DLLME is a powerful technique for the extraction of different analytes in a great variety of sample matrixes. DLLME allows an efficient miniaturization and simplification of the sample pre-treatment although its automation is clearly difficult. This difficulty arises from the unavoidable centrifugation step which is a typical off-line process. Some efforts have been made to avoid this step in order to open up a new horizon in DLLME automation. Berton *et al.* (Berton *et al.*, 2010b) have recently proposed an automatic TILDLME method, based on a flow injection manifold, for the determination of vanadium species in water samples. With no centrifugation the IL is recovered after the extraction using a florasil column, where the IL remains due to its high viscosity. The centrifugation step is also avoided

in the technique *one-step in-syringe ionic liquid-based dispersive liquid-liquid microextraction* (Cruz-Vera *et al.*; 2009b). In this technique the complete DLLME procedure is developed in a conventional plastic syringe. Once the cloudy solution is formed, the IL is recovered by the slight movement of the syringe plunger. This separation is possible due to the tendency of the IL to interact with the plastic walls of the syringe.

4.2 Ionic liquids in solid phase microextraction

Solid phase microextraction (SPME) was introduced by Pawliszyn and co-workers (Berladi & Pawliszyn, 1989) (Arthur & Pawliszyn, 1990) as a simple, time efficient and solvent-free technique. SPME integrates the sampling, isolation and preconcentration of the target analytes in one step as well as it allows the direct coupling with different instrumental techniques. SPME is based on the partition of the analytes of interest between the sample and a small amount of extracting phase dispersed and immobilized in a solid support and the subsequent thermal or solvent-based desorption (Cruz-Vera *et al.*, 2009c). SPME has been in a continuous evolution and different approaches, based on the sorptive phase minimization, have been developed.

Classical SPME used a fiber with an appropriate sorptive coating as extraction unit. The fiber is integrated in a syringe manifold which permits the development of the extraction as well as the subsequent injection of the analytes in the instrument, commonly a gas chromatograph. The fiber coating plays a key role on the extraction of the analytes. The ideal coating must fulfil some general requirements such as: (a) good affinity towards the target analytes in order to allow a good preconcentration; (b) thermal stability, especially when analytes desorption is assisted by an external heat source; (c) chemical stability, in particular when the desorption is performed by means of a chemical elution; (d) long life span; (e) low memory effect to avoid carry-over effects, (f) appropriate batch to batch reproducibility and (g) low price. As it is evident, the ideal coating does not exist and it should be selected according to the analytical problem under study. Moreover, the development of new coatings has turned into the goal of an extensive research in recent years. In this context, ILs can play an important role due to their characteristics that have been widely described in this chapter.

Liu and co-workers proposed for the first time the use of IL in a hybrid LPME-SPME approach (Liu *et al.*, 2005). In fact, $[\text{C}_8\text{MIM}][\text{PF}_6]$ is employed to cover a fused silica-fiber producing a disposable IL-coating. The IL-coating is of physical nature, without a covalent bonding, and it is performed by dipping a pretreated fused silica fiber into an IL solution in dichloromethane. After dipping, the fiber is dried removing the excess of dichloromethane, leaving a coating of $[\text{C}_8\text{MIM}][\text{PF}_6]$. The dipping and evaporating cycle is repeated three times in order to achieve the desired coating thickness. The use of IL in this type of coating presents some advantages such as: (a) due to its liquid nature, the coating can be easily removed using appropriate solvents; (b) due to its liquid nature, the coating presents higher diffusion coefficients which involve faster sorption kinetics and (c) due to its high viscosity, the IL can cover easily the fiber. Using this approach, the determination of benzene, toluene, ethylbenzene and xylene in paints has been achieved. Taking into account that the IL is only physically coated into the fiber, the volume of IL is reduced and therefore the sorption capacity limited. Hsieh *et al.* have proposed the use of nafion membranes as inner coating in order to maximize the volume of IL (Hsieh *et al.*, 2006). This polymeric membrane presents some anionic groups that may interact with imidazolium cations increasing the volume of

immobilized IL and providing a more stable coating. The proposed configuration used [C₈MIM][Tfo] as extractant for the determination of ultra traces of PAHs in water samples. The physical coating can be also employed in coated fused silica capillary previously etched with an appropriate solution. Etching process produces a rough capillary surface which is able to immobilize a higher volume of IL compared to the original bare fused silica capillary (Huang *et al.*, 2009). The use of elastomers has been proposed to improve coating consistency. For this purpose a mixture of IL and elastomers in a volatile solvent is placed in a beaker and heated until a suitable viscosity is achieved. In this moment, a fused silica fiber is dipped in this solution. Later on, the fiber is drawn and dried until the solvent is completely evaporated. After a cycle of dipping and evaporation, a coated fiber can be obtained. The IL is trapped in the polymeric coated but it remains in its liquid form. A 50 µm in thickness polymeric coating containing [C₄MIM][NTf₂] has been successfully applied to the determination of methamphetamine and amphetamine in forensic samples (He *et al.*, 2009b).

All the mentioned approaches correspond to a hybrid LPME-SPME strategy since typically SPME devices are employed while a liquid phase is used as extractant. The liquid nature of the extractant provides evident advantages (e.g faster sorption kinetics) but it limits the stability and reusability of the coatings. Polymeric ionic liquids (PILs) allow the development of classical SPME fibers providing better chemical and thermal stability compared to the above mentioned approaches (Zhao *et al.* 2008b). Moreover, PILs coatings present a longer life span (they can be used up to 150 times) and good reproducibility between fibers. This type of coatings are prepared with a dipping-evaporation process, similar to those described previously, using a solution of PILs in a volatile organic solvent. When the solvent is evaporated, a solid PIL-coating is obtained. SEM pictures of PILs coating are presented in Figure 2. PIL-based SPME fibers have been successfully employed for the extraction of a great variety of organic substances (López-Darias *et al.* 2010) or carbon dioxide (Zhao & Anderson, 2010).

ILs have been covalently bonded to a silica support in order to obtain a fiber coating (Wanigasekara *et al.* 2010). The IL is previously derivatized to obtain an appropriate reagent which is able to react with a silica substrate. As a result, the liquid state of the IL is lost but their inherent characteristics (such as low vapor pressure, chemical stability or affinity towards organic compounds) remain unaltered. This IL-silica coated fiber has been used for the extraction of polar compounds.

In the SPME context, ILs can be used as solvents for the synthesis of stationary phases for capillary microextraction (CME), a SPME mode based on the location of the sorptive phase in the inner volume of a fused- silica capillary. The IL may play a double role since it can act as a reaction solvent and/or porogen solvent. The use of IL as reaction solvent has some advantages such as: (a) the solvent can be recycled; (b) the solvent is thermo-stable in the temperature range in which the reaction takes place and (c) the reagents present a higher stability in ILs compared to other organic solvents. On the other hand, the use of ILs as porogens provides the final polymer with a higher porosity and therefore with a higher extraction efficiency. Moreover, the IL employed can be removed by a thermal treatment releasing a pure polymeric coating (Shearrow *et al.*, 2009a). The synthesis process is reproducible, both in run-to-run and capillary-to-capillary conditions. This approach has been successfully used for the fabrication of coatings focused on the extraction of polar substances, which is a challenge in the analytical chemistry context (Shearrow *et al.*, 2009b).

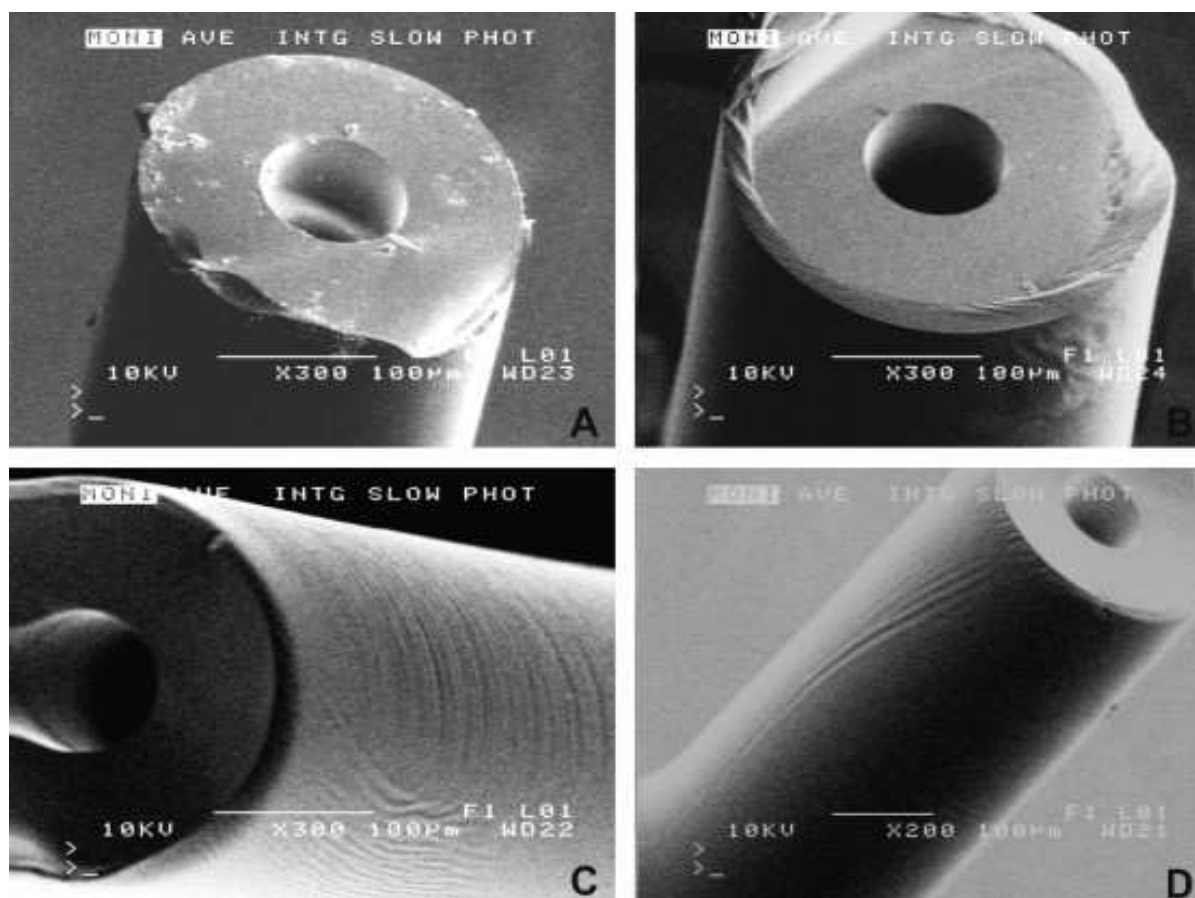


Fig. 2. Scanning electron micrographs of a 100- μ m inner diameter bare fused silica support (A) and various angles of the fused silica support coated with PIL (B–D). Figure from Zhao *et al.* (2008b) and reproduced with permission of Elsevier.

5. Ionic liquid-based sorbents for solid phase extraction

The use of a variety of sorbents in solid phase (micro)extraction techniques has several advantages compared to liquid phase (micro)extraction for sample clean-up and/or analyte(s) preconcentrations. In a previous section (see section 4.2) the main contributions of ILs to solid phase microextraction have been highlighted. However, ILs have also contributed to improve the sorbent capability of conventional sorbent materials in several ways, the most relevant of which are commented on.

The use of a soft functional material arising from the combination of ILs and carbon nanotubes, allowed by the specific interaction between imidazolium ion components of the IL and the p-electronic nanotube surface, has been described. The resultant gelatinous material, consisting of highly electroconductive nanowires and fluid electrolytes, has a high capacity to absorb/desorb analytes from a variety of liquid samples. This capacity is the result of the synergistic effect between ILs solvation power and the adsorption capacity of carbon nanotubes. This new sorbent has been successfully applied to the determination of traces of PAHs in river waters (Polo-Luque *et al.*, in press. a).

A conventional filter can be modified when a dissolution of carbon nanotubes in ILs is passed through it, leading to the stable retention of the nanotubes. This modified nanofilter has been applied to organic interference removal for the determination by non-aqueous

capillary electrophoresis (NACE) of imidazolium and pyridinium-based ionic liquids in river water (Polo-Luque *et al.*, in press. b). In a similar way, typical C₁₈ sorbents can be modified using a dissolution of carbon nanotubes in ILs; this sorbent has been used for the preconcentration and determination of sulphonamides in river water by capillary electrophoresis (Polo-Luque *et al.*, in press. c).

6. Ionic liquids in sample dissolution

Dissolution is the classical beginning in the analysis of solid and solid-liquid samples (Kellner *et al.*, 2005). The general objectives of this substep of the preliminary operations of analytical processes are: (a) to make the next detection step possible; (b) to improve sample homogeneity and, thus, to enhance reproducibility (and quality) of the results; (c) to enhance sensitivity; and (d) to contribute to the simplification. In many real cases, it is not an easy task to distinguish between dissolution and extraction (see part 4 of this chapter). In this context, solvent changeover can also be considered.

The capacity of dissolution of ILs is undeniable (Weingärtner, 2008) (see part 3 of this article). They have been involved as solvents in both, physico-chemical studies and analytical processes. The most relevant applications in the field of chemical analysis are commented on below.

6.1 Ionic liquids as matrixes for mass spectrometric analysis

The application of ILs as replacements for the conventional liquid or solid matrixes in Matrix Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS) has recently been recognized (Baker *et al.*, 2005). MALDI-MS is a powerful technique for determining high-molecular-weight compounds (e.g. biomacromolecules, synthetic polymers) as well as low-molecular weight compounds. The requirements of an effective matrix for MALDI-MS are as follows (Liu *et al.*, 2009b):

- To dissolve (liquid matrix) or co-crystallize (solid matrix) with the sample;
- To contain a chromophore to absorb laser light and promote ionization of the analyte;
- To remain in the condensed phase under high-vacuum conditions;
- To minimize or avoid thermal and chemical sample degradation.

As can be seen in Figure 3, the applications of ILs as matrixes for MALDI-MS satisfy almost all of these requirements, but their ability to promote ionization of the analyte is not accomplished in all cases since it depends on the type of analyte and IL. In addition, the great variety of ILs makes not possible to extend their general features to their role as matrixes in MALDI-MS analysis. A recent review (Tholey & Heinzle, 2006) compiles the most relevant aspects and fields of application of the topic.

One of the first attempts to use ILs as matrixes in MALDI-MS was reported by Armstrong's group using peptides, proteins and poly(ethylene glycol) (PEG-2000) as model analytes (Armstrong *et al.*, 2001). All of the IL-based matrixes showed excellent solubilizing properties and vacuum stability compared to other frequently employed solid and liquid matrixes. There are other recent papers aimed to compare ILs with conventional solid and liquid matrixes for a variety of sample-analyte-pairs (Mank *et al.*, 2004) (Zabet-Moghaddam *et al.*, 2004). Besides the properties pointed out by Armstrong in 2001 (Armstrong *et al.*, 2001) (see Figure 3), it has been demonstrated that liquid consistency of IL-matrix sample preparations considerably enhances MALDI-MS analysis in terms of shot-to-shot reproducibility, which is a bottle-neck in this technique.

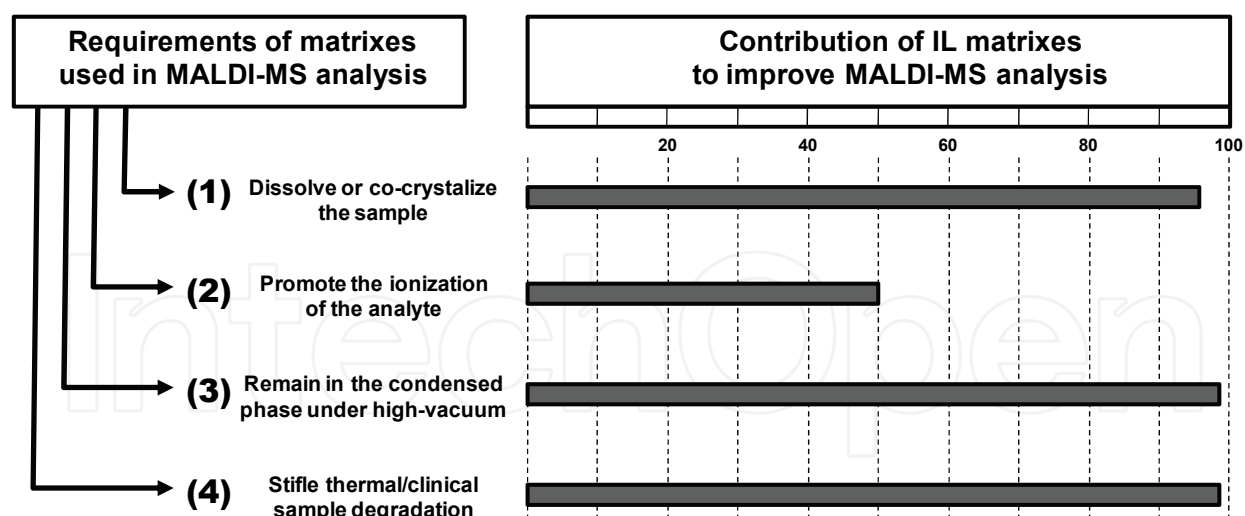


Fig. 3. Fulfillment by ILs of the basic requirements of matrixes in MALDI-MS analysis. For details, see text.

ILs as matrixes show also a synergy with the technique Matrix-Assisted Laser Desorption/Ionization-Time-of-Flight Mass Spectrometry (MALDI-TOF-MS) especially for screening purposes. Quantitative MALDI-TOF-MS using isotopic labeled internal standards and IL-based matrixes have been applied for the screening of 10 pyranose oxidase variants using aliquots of enzyme reaction mixtures without previous purification steps, which can be considered a relevant approach (Bungert *et al.*, 2004). In some cases, this technique is combined with a previous separation step. Such is the case of the fast screening of a mixture of low molecular weight compounds (three alkaloids, two anesthetics and one antibiotic) based on Thin-Layer Chromatography (TLC) followed by direct on-shot MALDI-TOF-MS identification with nearly matrix-free mass spectra using a UV-absorbing IL matrix. This technique is fast and sensitive and it requires little sample preparation and manipulation (Santos *et al.*, 2004).

6.2 Ionic liquids as solvents in molecular spectroscopy

Since 1986, ionic liquids have been demonstrated to be able to solvate a wide range of chemical species including organic, inorganic, metal complexes and organometallic compounds (Appleby *et al.*, 1986). The main advantages of the use of ILs as solvents in spectroscopy are (Koel, 2005): (a) they offer stability to a variety of species, particularly metal complexes; (b) they circumvent problems arising from solvation and solvolysis; and (c) they permit reliable UV-visible and IR solution spectra. Enhanced resolution and significant spectra shifts compared to those of the standards published have been observed. The spectra of the substance of interest obtained in ILs resemble to those recorded in solvents of low dielectric constants such as dichloromethane. The majority of publications on this topic are related to physico-chemical studies, but analytical processes can have benefit from having the analyte dissolved in an appropriate solvent, which can be achieved using extraction (see part 4 of this chapter) or solvent changeover by dissolution of the solid residue after the dryness of the first solvent employing heating or under a N₂ stream.

6.3 Ionic liquids as solvents in headspace gas chromatography

Owing to the inherent characteristics of ILs, such as non-volatility and heat stability, they can be used advantageously as solvents in headspace GC. The study performed by André

and co-workers (André *et al.*, 2005) is based on the use of three acidic, neutral and basic model analytes with boiling points above 200 °C which were dissolved in ILs; the analytes could be determined at the low-ppm level.

This approach has been successively applied to the determination of traces of low vapor pressure residual solvents in pharmaceutical drug products, a crucial aspect of their quality. Using the ionic liquid [C₄MIM][BF₄] as the matrix medium, residual solvents such as N-methyl-2-pyrrolidone and dimethylformamide in commercially-available pharmaceutical preparations have been determined using static headspace GC (Liu & Jiang, 2007).

6.4 Ionic liquids as solvents for nanoparticles

ILs are suitable solvents for the dissolution (extraction) of a great variety of nanomaterials both organic (e.g. carbon nanoparticles) and inorganic (e.g. gold nanoparticles, quantum dots, etc.). Solubility of nanoparticles in ILs can have different foundations, the most relevant being salting out effects and cation exchange processes, among others.

ILs can be exploited as useful tools for the analysis of environmental and biological samples for the determination of the pollution caused by manufactured nanomaterials and for clarification of their toxicity in humans, animals and plants. Some specific developments in this context have been described in the last years (Wei *et al.*, 2004) (Huang *et al.*, 2006) (Nakashima & Kawai, 2005).

In addition, ILs can be used for the characterization of nanomaterials. The fact that they can be easily solubilized in ILs facilitates the analysis. This is the case of the characterization of a commercial mixture of single-walled carbon nanotubes that can be characterized by Raman spectrometry as a single component. Other alternative consists of the initial sample dissolution in an IL ([C₄MIM][BF₄]) using ultrasonic energy, and the subsequent encapsulation of the nanotubes in sodium dodecylsulphate micelles. An aliquot of the dissolution is introduced in a capillary electrophoretic equipment and an electropherogram of 8 peaks (in less than 4 minutes) is obtained, which demonstrates the non-homogeneity of the original sample of carbon nanotubes (López-Pastor *et al.*, 2008).

7. Final remarks

Due to the fact that the majority of the preliminary operations of the analytical process rely on the use of solvents (e.g. dissolution, extraction, solvent changeover, etc), any contribution to minimize or to avoid the negative connotations of the conventional ones, both organic (e.g. hexane) or inorganic (e.g. HNO₃) should be welcome. Such is the case of ILs which, since two decades ago, have open up new perspectives and promising approaches in this field, enhancing the analytical properties (top, basic and productive) through the improvement of the sample preparation steps (Valcárcel & Rios, 1993). The main advantages of ILs as solvents in comparison with the traditional ones can be justified by their unique properties that have been described in part 1 of this chapter, being the most relevant for such purpose: solvent capability and tunability, thermal stability and very low vapor pressure, as well as their viscosity, density, surface tension, immiscibility with other solvents, etc.

There are presently several drawbacks that limit the use of ILs in Analytical Sciences, the most relevant being the following: (a) hygroscopy, which can led to the hydrolysis of the anion components; (b) impurity, traces of other compounds (e.g. water) that change the expected properties of ILs to be used for a fixed fit-for-purpose; (c) instability, arising from the decomposition of ILs under heating, ultrasonication or microwave energy, frequently

used in sample preparations; (d) alteration of the structure of the dissolved analytes (e.g. biomolecules); and (e) toxicity, despite the reputation of ILs as green solvents, recent studies evidence the relative toxicity of some of the ILs used in practice. The environmental fate and toxicity of ILs have been recently reviewed by Pham *et al* (Pham *et al.* 2010).

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