Ionic liquids in solid-phase extraction

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Supported ionic-liquid phases (SILPs), which favorably combine the properties of ionic liquids (ILs) with the advantages of solid supports, were presented in 2009 as an alternative material for solid-phase extraction (SPE). Since then, the number of SILPs used as SPE materials has increased and the results are promising.

This report covers various aspects of SILPs:

1. **the procedure for their preparation, which clearly depends on the support (based on silica or polymer) where the ILs are immobilized;**
2. **their interaction mechanisms, which are strongly linked to the SPE protocol and the target analytes; and,**
3. **their fields of application with a number of selected examples.**

This is the first review that exclusively describes all SILPs that have been developed to date as sorbents in SPE.

Keywords: Immobilizing support; Interaction mechanism; Ionic liquid (IL); Polymer-based support; Reversed phase (RP); Solid-phase extraction (SPE); Sorbent; Strong anion exchange (SAX); Supported ionic-liquid phase (SILP); Silica-based support

Abbreviations: See Appendix A on Annex abbreviation

1. Introduction

Sample pretreatment is one of the most important parts of the whole process of analysis. This stage includes analyte preconcentration and removal of interferences from complex matrices (e.g., environmental, biological and foodstuff samples) in order to make the analyte more suitable for separation and detection. In spite of the advances made in separation and detection techniques, sample preparation is a vital part of the analytical process, and it is essential if reliable results are to be achieved and instrument performance maintained [1]. Modern trends in analytical chemistry are towards simplification and miniaturization of sample preparation and minimization of the amount of organic solvent used.

Among the different extraction techniques, solid-phase extraction (SPE) is the most widely used sample-preparation technique for liquid samples. 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 sample-preparation techniques often therefore focuses on developing new materials to achieve higher selectivity and capacity of the technique.

The classic sorbents used in SPE are [2]:

(1) silica-based, modified with C_{18}, C_8, 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, hypercrosslinked sorbents have been developed, and, due to their ultra-high specific surface area of up to 2000 m^2/g, they provide a greater number of interaction points with the analytes to be extracted [3]. The hydrophobic structure of the original porous polymers has also been improved with the introduction of hydrophilic macroporous and hydrophilic hypercrosslinked sorbents. The hydrophilicity of the sorbents can be introduced through a hydrophilic precursor monomer or by chemically modifying the PS-DVB polymer skeleton [4].

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To improve selectivity, molecularly-imprinted materials (MIPs) were designed to overcome the limitation of the traditional restricted-access materials (RAMs) and immunosorbents (ISs). MIPs have specific cavities matched to template molecules and a retention mechanism based on molecular recognition, and they have been designed to interact selectively with the target compound(s) while removing all other analytes, including interferents [5].

In the context of the above challenges, research into SPE sorbents in recent decades has focused on improving capacity and selectivity within a single material, leading to the emergence of what are known as dual-phase or mixed-mode sorbents. These sorbents combine a silica or polymeric (the most common for promoting non-ionic interactions) skeleton with ionic groups, with two types of interactions available: reversed-phase (RP) (from the skeleton) and ionic-exchange (from the ionic groups). The typical classification in mixed-mode technology is by the type of ion group attached to the skeleton. Thus, these sorbents are classified as cationic or anionic and as strong or weak. The philosophy in mixed-mode sorbent technology is that, once the sorbent type is selected, careful choice of the pH and the solvent at each SPE step allows the matrix components and interferents to be eluted separately from the analytes of interest in the washing and elution steps, respectively.

In recent years, ionic liquids (ILs) have been immobilized onto silica or polymeric supports (known as supported IL phases – SILPs) in order to take advantage of the chemical functionality that ILs can impart and, as a result, new groups of stationary phases with different fields of application in different extraction techniques have emerged (e.g., SPME and SPE) and separation techniques (e.g., GC, LC and CE). SILPs can therefore be considered another class of sorptive material [6].

ILs are inorganic and organic salts with melting points below 100°C. Most ILs are a combination of organic cations (e.g., imidazolium, pyridinium, pyrrolidium, ammonium and phosphonium) and anions, which can be inorganic (e.g., Cl^-, PF_6^-, BF_4^- and NTf_2^-) or organic (e.g., trifluoromethylsulfonate or trifluoroethanoate). They have unique properties (e.g., negligible vapor pressure, high thermal stability, high viscosity, and good conductivity and solubility). One important feature of ILs is that varying the cation or anion can significantly affect their physical and chemical properties.

Consequently, combinations of different cations and anions result in a wide range of ILs with different properties, from which the ILs can be selected for specific applications. As a result of their exceptional properties, ILs have attracted interest as green solvents for chemical processes, including organic catalysis, and more recently, analytical chemistry and inorganic synthesis [7,8]. These liquids also exhibit a range of solvent properties, especially for the isolation of compounds from aqueous solutions, and they tend to be highly viscous, which limits their use as conventional solvents. In analytical chemistry, they are therefore good candidates for use in conventional solvent-based extraction, and as stationary phases in sorptive extractions [9].

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 [10–14] while others provide specific applications, mainly focused on stationary phases in separation techniques {e.g., gas chromatography (GC), liquid chromatography (LC) and capillary electrochromatography (CEC) [15,16]}, 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 microextraction (SPME) [17–20]}, or as part of sorptive material in extraction techniques {e.g., SPME [18,21] or SPE [16]}, 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.

With respect to sorptive extraction techniques, SILPs were first applied as an SPME coating in 2005, in a study where ILs were merely adsorbed on the fiber surface [22], which involved fiber re-coating after each extraction. Subsequently, in order to circumvent this limitation, polymeric ILs (PILs) were developed [23] by the Anderson research group, who recently extensively reviewed PILs as SPME coatings [21]. Some other recent reviews [18,20] were also devoted completely or partially to the use of PILs in SPME.

SILPs as SPE materials emerged later, in 2009. Since then, the number of applications has increased steadily. However, no comprehensive review completely dedicated to SILPs in SPE has yet been published, with only the very recent exception of the work by Vidal et al. [16], who reviewed SILPs together with other stationary phases for separation purposes.

The present review covers all the SILPs that have been used as sorptive materials in SPE to date. There is a description of the different synthetic routes for their preparation, a discussion of the interactions generated as well as the suitable SPE protocol for enhancing these interactions. A number of selected examples are then given of applications of SILPs in SPE in order to illustrate their benefits and limitations.

2. Preparation of supported ionic-liquid phases (SILPs)

The SILPs in SPE can be classified as silica- or polymer-based, depending on where they are supported. The first