Ionic liquid and polymeric ionic liquid coatings in solid-phase microextraction

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Sample preparation is often considered to be a bottleneck in most analytical methods. Solid-phase microextraction (SPME) consolidates sampling and sample preparation into one step. The unique properties of ionic liquids (ILs) and polymeric ILs (PILs) have been exploited as sorbent coatings in SPME. Due to their tunable structures, these materials exhibit unique selectivity for various analytes.

This article discusses the overall progression of IL and PIL-based sorbent coatings in SPME. The structural engineering and design of selective sorbent coatings is discussed to demonstrate the versatility of these materials in numerous applications.

Keywords: Dip coating; Fiber surface; Ionic liquid (IL); Polymeric ionic liquid (PIL); Sample preparation; Sampling; Selectivity; Solid-phase microextraction (SPME); Solvent; Sorbent coating

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1. Introduction

Solid-phase microextraction (SPME) was introduced by Pawliszyn and co-workers in the early 1990s as a technique that combines sampling and sample preparation into one step [1]. It has been widely applied due to its simplicity, cost-effectiveness, and solvent-free properties [2]. SPME is a non-exhaustive extraction technique and is based on the partitioning of analytes in a sample matrix to a sorbent phase, which is often coated on a support [2,3]. Analytes are extracted by three different modes, namely, headspace SPME (HS-SPME), direct-immersion SPME (DI-SPME) and membrane-protected SPME (MP-SPME).

In HS-SPME, the sorbent coating is exposed to the headspace of the sample solution containing the analyte(s) of interest. Exposing the coating to the headspace allows for the rapid extraction of volatile analytes without the need to introduce the coating to the matrix. For analytes that are less volatile or possess high affinity to the matrix, DI-SPME or MP-SPME may be employed, wherein the sorbent coating is immersed in the sample solution itself [4]. Subsequent to extraction, analytes are desorbed from the fiber coating and subjected to separation by gas chromatography (GC) or high-performance liquid chromatography (HPLC) [5].

SPME has expanded into multiple scientific disciplines including trace-level analyses of analytes in food, pharmaceutical, environmental, biological and other real-world samples [6–9]. At present, there are a number of commercially-available SPME sorbent coatings that possess broad selectivity based largely on their polarity for different analyte classes. However, there is a lack of coatings possessing high selectivity towards specific classes of analytes. As the applicability of SPME continues to grow to real-world samples in which analytes are often at extremely low concentrations, it is imperative to investigate new sorbent-coating technologies that allow the analyst greater control over analyte selectivity.

Ionic liquids (ILs) have previously been exploited as extractants, porogens, mediators, and/or solvents in various microextraction techniques [10]. Specifically, within the past seven years, ILs and polymeric ILs (PILs) have been promising sorbent-coating materials that can be designed to exhibit high selectivity for target analytes [11]. ILs are salts with

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melting points at or below 100°C and are comprised of organic cations and organic/inorganic anions. They possess unique physicochemical properties (e.g., high thermal stability, tunable viscosity and solvation capabilities) and negligible vapor pressures. The main advantage of using ILs as SPME sorbent coatings is the ability to incorporate various substituents into the IL structure, so as to enhance specific interactions between the IL coating and target analytes.

PILs are polymers synthesized from IL monomers. They possess a number of advantages over ILs when used as coatings in SPME. PILs often possess higher viscosity and greater mechanical strength compared to ILs while exhibiting similar extraction selectivity [12]. PIL-based coatings are not prone to flowing off the fiber support particularly at high GC desorption temperatures. As a result, PIL-based coatings do not need to be recoated after each extraction and desorption step. DI-SPME is also possible for certain classes of hydrophobic PIL-based coatings [11].

This article focuses primarily on the progression of IL and PIL-based SPME sorbent coatings from the initial stages to the most recent advancements. We focus attention upon structural tuning and enhancement of various aspects of coating technology, including selectivity, physicochemical and mechanical stability, and fiber lifetimes. We highlight the applicability of these sorbent coatings by discussing the types of analytes and matrices that have been studied. Finally, we discuss the current limitations of IL/PIL-based coatings.

2. Advances in IL-based SPME sorbent coatings

2.1. Studies on selectivity and fiber surface modifications

The following sections encompass studies that involved utilizing ILs as sorbent coatings in SPME. For convenience, studies employing these types of coatings are summarized in Table 1.

Liu and co-workers initially applied ILs as SPME sorbent coatings [13]. The 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]) IL was used for the headspace extraction of benzene, toluene, ethylbenzene, and xylenes (BTEX) in paints, coupled with GC/flame ionization detection (GC/FID). The viscous IL-based coating allowed for extraction times faster than solid sorbent phases. Also, the dip-coated IL was used as a disposable SPME coating, which avoided analyte carry-over [13].

Recently, another study using an analogous dip-coating method for the 1-butyl-3-methylimidazolium PF_6 ([C_4MIM][PF_6]) IL was explored by Ho and co-workers [14]. Good extraction efficiency and precision were observed when the coating was applied to the analysis of chlorophenols (CPs) in landfill leachate. Unlike the single-use IL coating reported by Liu et al. [13], fibers were reported to be reusable up to 120 times.

Amini and co-workers explored the selectivity of four different ILs {namely, 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4MIM][BF_4]), 1-ethyl-3-methylimidazolium ethylsulfate ([C_2MIM][$EtSO_4$]), [C_8MIM][BF_4], and [C_8MIM][PF_6]} for the extraction of methyl tert-butyl ether (MTBE) in gasoline samples [15]. The disposable IL coatings were loaded on silica-fiber supports and prepared for headspace extraction. A comparison in extraction efficiency showed that the [C_8MIM][BF_4] coating exhibited the highest sensitivity for MTBE.

In order to achieve a higher, more homogeneous IL loading, Nafion was employed in a fiber-pretreatment method [16]. A stable IL coating was achieved on the Nafion pre-coated support as a result of the electrostatic interaction at the IL-Nafion interface. The fiber was applied in the analysis of polycyclic aromatic hydrocarbons (PAHs) in water samples. The extraction efficiencies of three ILs {namely, 1-octyl-3-methyl-imidazolium trifluoromethanesulfonate ([C_8MIM][TfO]), 1-benzyl-3-methylimidazolium trifluoromethanesulfonate ([BeMIM][TfO]), and 1-methyl-3-phenylpropylimidazolium trifluoromethanesulfonate ([PhproMIM][TfO]} were compared wherein the [C_8MIM][TfO] IL coating exhibited the highest extraction efficiency.

One disadvantage to using the Nafion-polymer membrane was that it may undergo hydrophobic interaction with PAHs, resulting in unwanted interference during the adsorption/desorption process [16,17]. Huang and co-workers developed a wet-etching method to pretreat the silica support using ammonium hydrogen difluoride prior to coating [17]. This etching technique increased the surface area of the fiber and allowed for a more mechanically stable IL coating on the fiber support, as shown in Fig. 1. Three silica supports, namely, etched, Nafion-supported and bare fused silica were coated with the [C_4MIM][PF_6] IL and applied to the headspace extraction of PAHs. The etched fiber exhibited the highest extraction efficiencies for the analytes studied, followed by the Nafion-supported fiber, which exhibited extraction efficiencies 3–5-fold higher than the bare fiber. The superior extraction efficiency of the etched-IL coated fiber was attributed to the ability to load a larger volume of IL onto the rough surface of the support.

2.2. Substrate-bonded IL sorbent coatings for improved chemical and mechanical stability

In order to allow for improved chemical, thermal, and/or mechanical stability, surface-modification techniques have been developed to immobilize the IL to a fiber substrate. The following studies describe the fabrication of substrate-bonded IL sorbent coatings and their applications in SPME. For convenience, Table 2 lists the various coating immobilization methods used along with potential advantages and disadvantages.