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Tuning the selectivity of polymeric ionic liquid sorbent coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase microextraction

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ABSTRACT

A new generation polymeric ionic liquid (PIL), poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm$^+$ NTf$_2^-$)), was synthesized and is shown to exhibit impressive selectivity towards the extraction of 12 polycyclic aromatic hydrocarbons (PAHs) from aqueous samples when used as a sorbent coating in direct-immersion solid-phase microextraction (SPME) coupled to gas chromatography (GC). The PIL was imparted with aromatic character to enhance π–π interactions between the analytes and the sorbent coating. For comparison purposes, a PIL with similar structure but lacking the π–π interaction capability, poly(1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly(HDIm$^+$ NTf$_2^-$)), as well as a commercial polydimethylsiloxane (PDMS) sorbent coating were evaluated and exhibited much lower extraction efficiencies. Extraction parameters, including stir rate and extraction time, were studied and optimized. The detection limits of poly(VBHDIm$^+$ NTf$_2^-$), poly(HDIm$^+$ NTf$_2^-$), and PDMS coatings varied between 0.003–0.07 μg L^{-1}, 0.02–0.6 μg L^{-1}, and 0.1–6 μg L^{-1}, respectively. The partition coefficients (log K_{fs}) of eight PAHs to the three studied fiber coatings were estimated using a static SPME approach. This study represents the first report of analyte partition coefficients to any PIL-based material.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. Studies have shown that they distribute in a variety of environmental matrices worldwide [1,2]. Formation of PAHs is mainly due to incomplete combustion of organic compounds. Common sources include engine exhaust from automobiles [3] and smoke of industrial [4], municipal, and domestic origins as well [5]. Because of their toxic and carcinogenic effects, PAHs have been listed as priority pollutants in wastewater, groundwater, hazardous solid waste, soil and sediments by the United States Environmental Protection Agency (EPA) [6,7]. Due to the low concentration of PAHs in the environment, analytical methods aimed at analyzing these compounds include isolation and pre-concentration steps prior to chromatographic separation. Conventionally, PAHs can be preconcentrated and extracted by means of liquid–liquid extraction (LLE) and solid-phase extraction (SPE). However, LLE is tedious, time consuming, and requires large amounts of organic solvent. SPE is more time efficient, but it still requires organic solvent for the elution step.

Solid-phase microextraction (SPME) has received considerable attention due to its high sensitivity, simplicity, and lacking requirement of organic solvents [8]. This technique has gained increasing utility in trace analysis within many areas of research, including environmental [9], food [10], and pharmaceutical analysis [11]. SPME has been used successfully for the determination of PAHs [12,13]. Doong et al. investigated the performance of five SPME fibers for the extraction of PAHs including: 100, 30, 7 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), and 65 μm Carboxen-PDMS and found that the 100 μm PDMS fiber exhibited higher affinity to the higher-ring containing PAHs while the 85 μm polyacrylate (PA) was more suitable for PAHs possessing smaller ring structures [14]. Aguinaga et al. found the intermediate polarity polydimethylsiloxane–divinylbenzene (PDMS/DVB) sorbent coating (65 μm) to be more suitable than a 100 μm PDMS and a 85 μm PA coating due to the π–π interactions imparted by the DVB copolymer [15].

In addition to commercial fibers, considerable effort has been devoted to developing new coatings capable of improving the extraction efficiency of PAHs. Bagheri et al. reported the electrochemical deposition of polyaniline films as a SPME extraction phase in the determination of five PAHs [16]. Coupled with GC–MS, naphthalene, acenaphthylene, acenaphthene, fluorene, and anthracene were extracted with limits of detection (LODs) in the range of 0.1–6 pg mL^{-1}. The low LODs were attributed to the high surface

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area and π–π interactions imparted by structure of polyaniline. Recently, Yan and co-workers reported the use of etched stainless steel wire to extract PAHs, and the new fiber showed much higher enrichment factors than PDMS and PDMS/DVB fibers based on donor–acceptor interactions [17]. Coupled with GC–FID, Jiang's group reported the extraction of naphthalene, fluorene, anthracene, and fluoranthene using TiO_2 nanotubes as SPME coating materials with LODs of 0.1–0.01 μg L^{-1} [18]. Carbon nanotubes were also reported to exhibit higher extraction efficiency than the commercial PDMS coating in the extraction of PAHs [19]. By incorporating phenyl groups into sol–gel solutions, Bianchi and co-workers improved the extraction of PAHs in terms of extraction efficiency, thermal and chemical stability [20]. Coupled with GC–MS, the detection limits for many PAHs were two-fold lower than those obtained by a 7 μm PDMS fiber. By introducing cyclodextrin in the PDMS network, Hu et al. fabricated a SPME membrane capable of extracting PAHs [21]. Coupled with GC–MS, detection limits ranged from 0.01 to 0.2 μg L^{-1}.

Ionic liquids (ILs) have emerged as an increasingly popular class of solvents for various applications within analytical chemistry [22]. The tunable solvation interactions make them useful as stationary phases in GC [23–25], and high performance liquid chromatography (HPLC) [26,27], matrices in matrix-assisted laser desorption/ionization (MALDI) mass spectrometry [28], liquid–liquid extraction [29,30], dispersive liquid–liquid microextraction [31], and single drop microextraction [32,33]. Their high viscosity, high thermal stability, and tailored water-immiscibility coupled with their minimal vapor pressure promotes the formation of stable coatings for SPME [34–39]. IL-based SPME coatings provide a new avenue in the search for additional classes of highly efficient and selective sorbent coating materials in SPME. Our group has recently introduced SPME coatings based on polymeric ionic liquids (PILs) [37–39]. Due to their high thermal stability and resistance to flowing at elevated temperatures, PIL-based SPME coatings can be re-used while also exhibiting long lifetimes when they are coupled with GC. In addition, the fibers exhibit exceptional extraction-to-extraction reproducibility.

One of the remarkable advantages of using ILs as separation media lies in the ease of IL/PIL functionalization, making them tunable in providing desired selectivity and sensitivity towards target analytes [32,40]. In this work, a new generation of structurally designed PIL-based SPME coatings was synthesized and used for the extraction of PAHs. To improve the extraction efficiency of these analytes, the PIL was functionalized with benzyl groups capable of imparting π–π interactions between the analyte and the sorbent coating. Due to the stronger hydrophobic and enhanced π–π interactions, the new PIL sorbent coating exhibits significantly higher sensitivity and lower detection limits than a similar PIL lacking benzyl groups and much higher sensitivity than a commercial PDMS fiber of similar film thickness. To further understand the unique selectivity and sorption behavior of the PIL coatings, the static SPME method [41–43] was used to estimate the partition coefficients of PAHs to the two PIL-based sorbent coatings as well the PDMS sorbent coating.

2. Experimental

2.1. Chemicals and reagents

The following PAH standards were obtained from Supelco (Bellefonte, PA, USA): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene. The reagents imidazole, 1-bromohexadecane (97%), 4-vinylbenzyl chloride (97%), acrylonitrile (>99%), and 2,2′-azo-bis(isobutyronitrile) (AIBN) were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from SynQuest labs (Alachua, FL, USA). Chloroform, methylene chloride, hexane, acetone, cyclohexane, and methanol (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) and was used in the preparation of all aqueous solutions.

For SPME experiments, all of the PAHs investigated were dissolved individually in acetone to prepare standard solutions with concentrations of 2000 or 1000 μg mL^{-1}. These standard solutions were used to prepare stock solutions: solution A containing 500 μg mL^{-1} of naphthalene, acenaphthylene, acenaphthene and fluorene; solution B containing phenanthrene, anthracene and fluoranthene at concentrations of 200 μg mL^{-1}; and solution C containing pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene at concentrations of 10 μg mL^{-1}. Acetone was used to prepare diluted working solutions. All stock solutions were stored at 4 °C. The working solutions were prepared by spiking a certain amount of the stock solutions into 19.70 mL of deionized water within a 20 mL sampling vial.

2.2. Quantification of FID response

The external calibration method was used to determine the detector response for all analytes examined in this study. All of the PAHs were dissolved individually in cyclohexane to prepare standard solutions of 20 μg mL^{-1}. Three stock solutions with concentrations of 5 μg mL^{-1} for each analyte were prepared: solution 1 containing naphthalene, acenaphthylene, acenaphthene, and fluorene; solution 2 including phenanthrene, anthracene, fluoranthene, and pyrene; solution 3 containing benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene. Cyclohexane was used to prepare diluted working solutions. Calibration curves of the analyte peak area (from FID response) versus the mass of PAHs injected onto the column were generated by injecting 1 μL of a standard mixtures through an autosampler using identical inlet and column conditions as to those carried out during SPME desorption. The FID response from the direct liquid injection of the standard solutions was used to estimate the amount of analyte extracted by the three different SPME sorbent coatings examined in this study.

2.3. Materials

Fused silica capillary (0.10 mm I.D.) and amber glass vials (20 mL) with PTFE/Butyl septa screwcaps were obtained from Supelco (Bellefonte, PA, USA). A 7 μm PDMS fiber and a manual SPME holder were also purchased from Supelco. The poly(1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) (poly($HDIm^+$ NTf_2^-)) PIL was prepared using previously published procedures [37]. A home-made SPME device was constructed by purchasing a 5 μL syringe from Hamilton (Reno, NV, USA) and the syringe re-assembled by discarding the stainless steel fiber on the plunger and replacing it with a fused silica capillary affixed by epoxy glue (GC Electronics, IL, USA). The end of the capillary was sealed by a microflame torch and the outer 1 cm of the polyimide coating was removed. The bare fiber segment was washed with methanol, acetone, hexane, and methylene chloride before coating. PTFE stir bars were obtained from Fisher Scientific and were used to perform all extractions at an optimized stir rate on a Corning stir plate (Nagog Park Acton, MA, USA). An auto injector (7683B Series) purchased from Agilent (Agilent Technologies, Palo Alto, CA, USA) was employed for all direct liquid injection experiments.

2.4. Instrumentation

All separations were performed using an Agilent 6850N gas chromatograph equipped with a flame ionization detector (FID). A 0.75 mm I.D. liner was used to introduce the sample to the column. Helium was used as the carrier gas and maintained at a constant flow rate of 1 mL min^{-1}. All separations were performed using a HP-5 capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness) purchased from Agilent Technologies. Desorption of the fibers into the injection port was carried out in the splitless mode at 250 °C for 5 min. The following temperature program was used for the chromatographic separation of the mixture: initial temperature of 80 °C was held for 1 min and increased to 160 °C at 25 °C min^{-1}, from 210 °C at 10 °C min^{-1} increased to 216 °C at a ramp of 3 °C min^{-1}, increased to 246 °C at 10 °C min^{-1}, and then finally the oven temperature was raised to 300 °C at 3 °C min^{-1} and held for 10 min. The temperature of the detector was set at 300 °C. All scanning electron micrographs were obtained using a Hitachi S-4800 High Resolution Scanning Electron Microscope.

2.5. Synthesis of benzyl-functionalized polymeric ionic liquid SPME sorbent coating

The poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (poly(VBHDIm$^+$ NTf_2^-)) PIL was synthesized as shown in Fig. 1. To a 50-mL round-bottom flask, 0.1 mol of imidazole and 0.13 mol of acrylonitrile were added to 10 mL of methanol. The mixture was heated to 45 °C for 5 h under nitrogen. Methanol and excess acrylonitrile were subsequently removed under vacuum to obtain compound **1**. This compound was dissolved in 30 mL of chloroform followed by the addition of 0.1 mol of 1-bromohexadecane. The resulting solution was refluxed overnight to obtain compound **2**. Then, 40 mL of a 15% (w/w) NaOH aqueous solution was added. The mixture was stirred overnight at room temperature. The chloroform layer was separated using a separatory funnel and the organic layer was washed with water five times in order to eliminate the base and other impurities. Chloroform was subsequently removed and the residue dried under vacuum to yield compound **3**. The product was re-dissolved in chloroform and one molar equivalent of 4-vinylbenzyl chloride was added. The solution was refluxed overnight to yield compound **4**. The polymerization reaction was commenced by introducing AIBN (1% by weight) under the protection of N_2 and refluxed for 3 h. Finally, the halide counteranion was exchanged to [NTf_2^-] by metathesis anion exchange. In this procedure, 0.1 mol of lithium bis[(trifluoromethyl)sulfonyl]imide dissolved in 30 mL of water was added to the polymer/chloroform solution. The two-phase solution was stirred at room temperature for 3 days and the chloroform layer separated by separatory funnel. The chloroform solution was then washed with water multiple times to remove all halide residues from the product followed by the removal of chloroform under vacuum to yield compound **5**. The ^{1}H NMR spectra of compounds **4** and **5** as well as the poly(HDIm$^+$ NTf_2^-) PIL (produced following procedures from Ref. [37]), along with corresponding peak assignments, are shown in Fig. 2. Successful polymerization was evidenced by the disappearance of the proton signals originating from the vinyl group.

The IL monomer and polymer and all intermediate products were characterized using ^{1}H NMR carried out using Varian VXRS-400 MHz and UNITY INOVA-600 MHz spectrometers. ^{1}H NMR [δ ppm relative to TMS]: Compound **1** (400 MHz, d_6-DMSO): 7.470 (s, 1 H), 7.005 (s, 1H), 6.712 (s, 1H), 4.023 (t, 2H), 2.797 (t, 2H); Compound **2** (400 MHz, $CDCl_3$): 9.984 (s, 1H), 7.945 (s, 1H), 7.244 (s, 1H), 4.750 (t, 2H), 4.060 (t, 2H), 3.198 (t, 2H), 1.712 (m, 2H), 1.036 (m, 26H), 0.647 (m, 3H); Compound **3** (400 MHz, $CDCl_3$): 7.932 (s, 1H), 7.086 (s, 1H), 6.920 (s, 1H), 3.974 (t, 2H), 1.754 (m, 2H), 1.208 (m, 26H), 0.816 (t, 3H); Compound **4** (600 MHz, d_6-DMSO): 9.401 (d, 1H), 7.857 (m, 2H), 7.541 (m, 4H), 6.773 (dd, 1H), 5.891 (d, 1H), 5.424 (m, 2H), 5.330 (dd, 1H), 4.162 (t, 2H), 1.755 (m, 2H), 1.227 (m, 26H), 0.830 (t, 3H).

2.6. Preparation of SPME fibers and extraction procedures

The coating of the SPME fiber followed the procedures described previously [37,38]. Briefly, the poly(VBHDIm$^+$ NTf_2^-) and poly(HDIm$^+$ NTf_2^-) PILs were diluted in chloroform to prepare a coating solution with a ratio of 1:1 (v/v). The bare fiber was then dipped into the solution and slowly removed. After coating, the fiber was dried in the air for 10 min before it was retracted back into the needle. The fiber was conditioned in the GC injection port for 5 min at 250 °C prior to performing extractions.

To carry out the extractions, 19.70 mL of Milli-Q water and an appropriate amount of stock solution were placed in 20 mL amber glass sampling vials. The vial was immediately closed with a screw-cap after introducing a magnetic stir bar. The needle of the SPME device was pierced through the septum of the vial and the fiber then exposed directly into the solution. Immediately, the extraction was initiated by stirring the solution under the optimized conditions. After the extraction, the fiber was withdrawn back into the syringe and immediately transferred to the GC injection port for thermal desorption. In order to remove any carryover effects of PAHs with the sampling vials used in this study, they were first cleaned by sonicating with detergent for 2 h and then with deionized water for four 1 h cleaning increments. The vials were then kilned at 500 °C for longer than 4 h before use. The stir bars used in this study were sonicated in acetone for over 30 min and then rinsed with fresh acetone. They were then air dried for over 2 h before use. Carryover was examined after performing extractions at the highest concentrations on the calibration curves, namely 1.7 mg L^{-1} of naphthalene, acenaphthylene, acenaphthene and fluorene; 130 μg L^{-1} of phenanthrene, anthracene, and fluoranthene; 9 μg L^{-1} of pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene, by reinserting the SPME fiber in the injector for another 5 min after each run. The highest carryover was found to be less than 4%.

2.7. Partition coefficient estimation using SPME

The amount of analyte extracted can be determined by Eq. (1) [45],

$$n_f = \frac{K_{fs} V_f n_0}{K_{fs} + V_s} \quad (1)$$

where n_0 is the initial amount of analyte in the sample, n_f is the amount of analyte on the fiber after equilibrium, V_s is the volume of matrix, and V_f is the volume of the fiber coating. By rewriting Eq. (1), the partition coefficient (K_{fs}) can be calculated directly according to Eq. (2).

$$K_{fs} = \frac{V_s}{V_f((n_0/n_f) - 1)} \quad (2)$$

In the determination of partition coefficients for this study, the sample volume (V_s) was maintained at 19.70 mL. The initial mass of the analyte was 118.2 ng for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 59.1 ng for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene. For the 7 μm PDMS fiber, the volume of sorbent material (V_f) is 0.026 μL, as reported by the manufacturer. The volume of the PIL sorbent layer for the poly(VBHDIm$^+$ NTf_2^-) and poly(HDIm$^+$ NTf_2^-) PILs was calculated as a cylindrical layer of polymer on the fused silica support possessing an outer diameter of 237 μm and length of 1 cm. The film

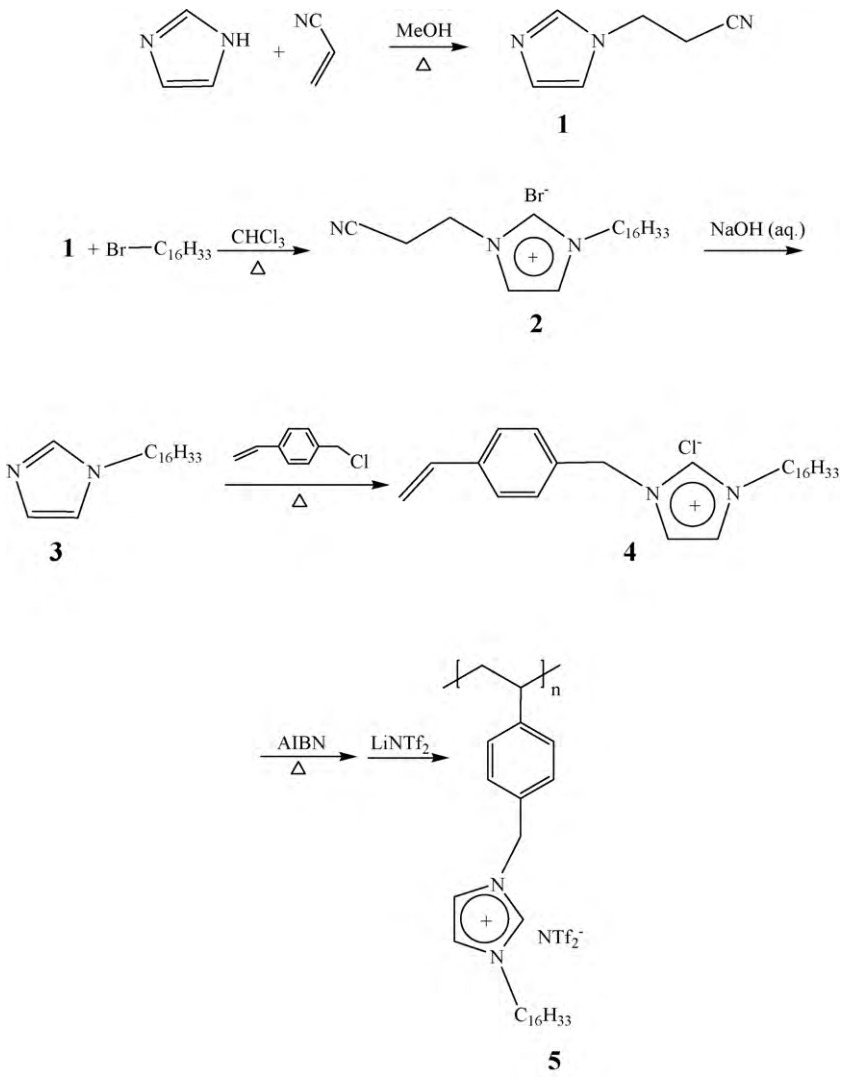

Fig. 1. Synthetic route used to prepare the poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide PIL.

thickness for both of the PILs was estimated to be in the range of 12–16 μm, as determined by scanning electron microscopy (SEM). Representative SEM photos of fibers containing the two PIL coatings are supplied as supplementary data. For estimation purposes, 12 μm was used as the approximate film thickness which yielded a V_f of 0.094 μL for both of the PIL-based fibers.

3. Results and discussion

3.1. Development of PAH selective PIL-based coatings

Due to the low vapor pressure and high boiling point of PAHs, direct-immersion SPME at room temperature provides higher extraction efficiency compared to headspace SPME. Therefore, sorbent coating materials must be sufficiently hydrophobic to avoid dissolution of the coating during prolonged sampling. For this reason, the PIL introduced in this study was synthetically designed to possess a long hydrocarbon chain structure in addition to containing the non-coordinating bis[(trifluoromethyl)sulfonyl]imide [NTf_2^-] anion, both of which impart the PIL with enhanced hydrophobicity. The poly(HDIm$^+$ NTf_2^-) PIL (see Fig. 2C) has been shown previously to exhibit higher extraction efficiency of PAHs compared to the PDMS sorbent coating [44]. In order to further increase the selectivity of the sorbent coating, additional aromatic character (in the form of benzyl groups) was introduced into the PIL structure, as shown in Fig. 1. It was hypothesized that addition of π-electrons to the PIL could enhance the extraction efficiency of PAHs by promoting stronger π–π interactions between the PIL sorbent coating and the analyte. As shown in Fig. 2, the only difference between the two PILs examined in this study is the presence of benzyl moieties within the chemical structure of the poly(VBHDIm$^+$ NTf_2^-) PIL. The imidazolium cation core, length of aliphatic hydrocarbon substituent, and anion are identical for the poly(VBHDIm$^+$ NTf_2^-) and poly(HDIm$^+$ NTf_2^-) PILs.

3.2. Optimization of stir rate and sampling time

Agitation is a very important factor that affects extraction in SPME. Good agitation accelerates the diffusion and mass transfer of analytes from the aqueous solution to the extraction phase and consequently reduces the extraction time. Fig. 3 shows the dependence of stir rate on the extraction peak areas of PAHs using a range from 200 to 1000 rpm for the poly(VBHDIm$^+$ NTf_2^-) PIL fiber. The extraction peak areas for all analytes reached equilibrium when the stir rate was higher than 800 rpm. Therefore, 800 rpm was chosen as the optimized stir rate for subsequent studies.

Sampling time is another decisive factor in achieving distribution equilibrium of the analyte between the sample and the

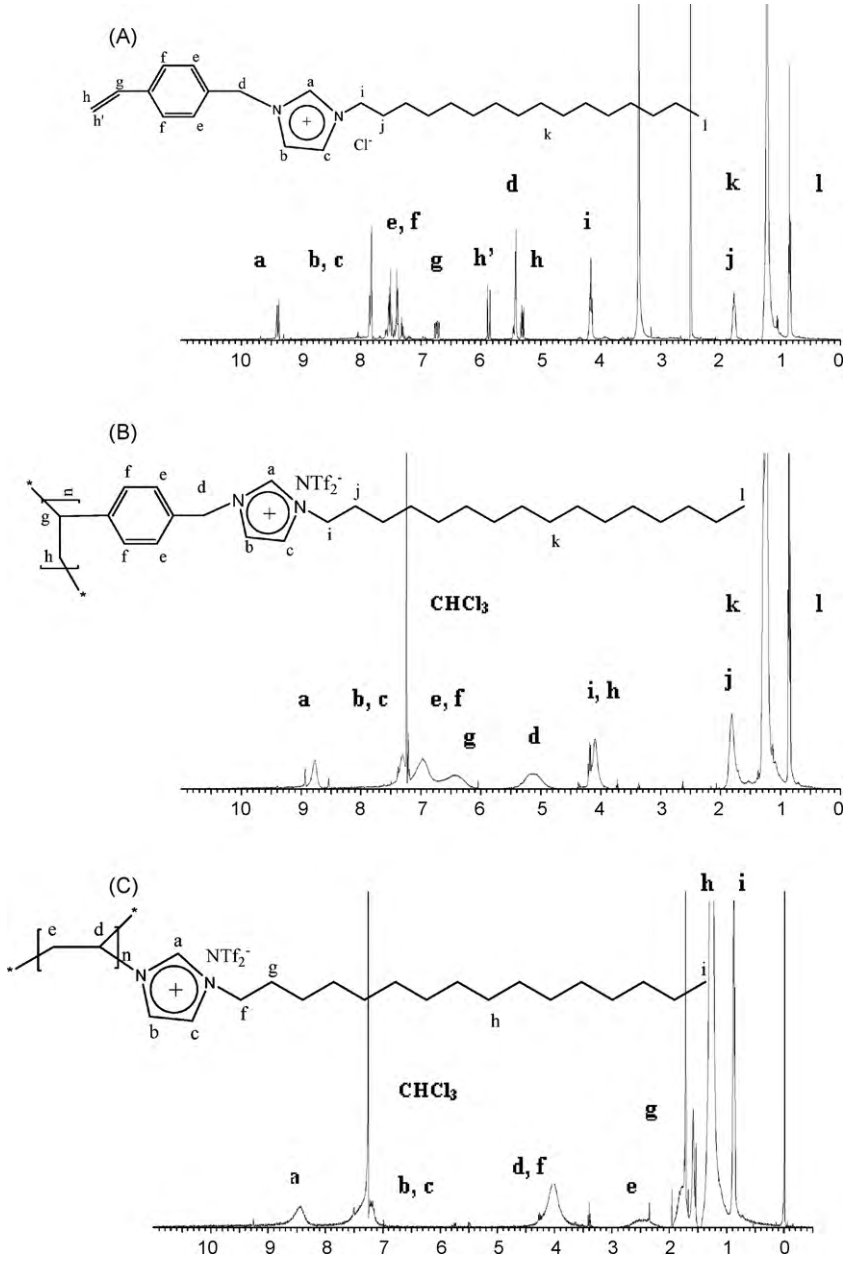

Fig. 2. ^{1}H NMR spectra of (A) 1-(4-vinylbenzyl)-3-hexadecylimidazolium chloride in d_6-DMSO, (B) poly(VBHDIm$^+$ NTf$_2^-$) in $CDCl_3$, and (C) poly(HDIm$^+$ NTf$_2^-$) in $CDCl_3$.

extraction phase. SPME extractions were carried out at various extraction times using a stir rate of 800 rpm. Fig. 4 shows the peak area versus sampling time for the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber. All of the PAHs reached equilibrium in approximately 45 min. When an extraction time longer than 45 min was applied, the extraction peak areas for the PAHs slightly decreased and leveled off. Thus, 45 min was chosen as the best extraction time for the PIL fiber.

Sorption-time profiles for the poly(HDIm$^+$ NTf$_2^-$) PIL and PDMS (7 μm) fibers were also generated using a stir rate of 800 rpm, as shown in Figs. 5 and 6, respectively. Due to the lower extraction efficiencies of these two fibers for the PAHs, the concentration of the analytes was increased six-fold in order to achieve reasonable extraction for further optimization. Most of the PAHs reached equilibrium using the poly(HDIm$^+$ NTf$_2^-$) PIL fiber (Fig. 5) in approximately 40 min, except for fluorene, acenaphthene and acenaphylene which required longer than 60 min to reach equilibrium. For the PDMS fiber (Fig. 6), most of the analytes reached equilibrium in approximately 30 min. Therefore, 40 and 30 min were chosen as the optimized fiber exposure times for the poly(HDIm$^+$ NTf$_2^-$) PIL and PDMS fibers, respectively, and were used for subsequent calibration studies.

Different extraction behaviors were observed for the three coatings in terms of the extraction time needed for most of the analytes to reach equilibrium: approximately 45 min for the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber, 40 min for the poly(HDIm$^+$ NTf$_2^-$) PIL fiber, and 30 min for the PDMS fiber. This difference can be partly explained by the varying film thicknesses and properties of the sorbent coatings. The thinner film thickness of PDMS (7 μm) provided shorter equilibration times, while the slightly thicker PIL-based coatings rendered longer equilibration times. Compared with the PDMS fiber, the higher extraction peak areas for the two PIL fibers indicated the higher affinity of the fibers towards PAHs. The phenomenon in which the extraction peak areas decreased after the fiber was saturated for the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber and PDMS fiber may be attributed to the adsorption of these PAHs on the wall of the sampling vials. Given the low concentrations of the

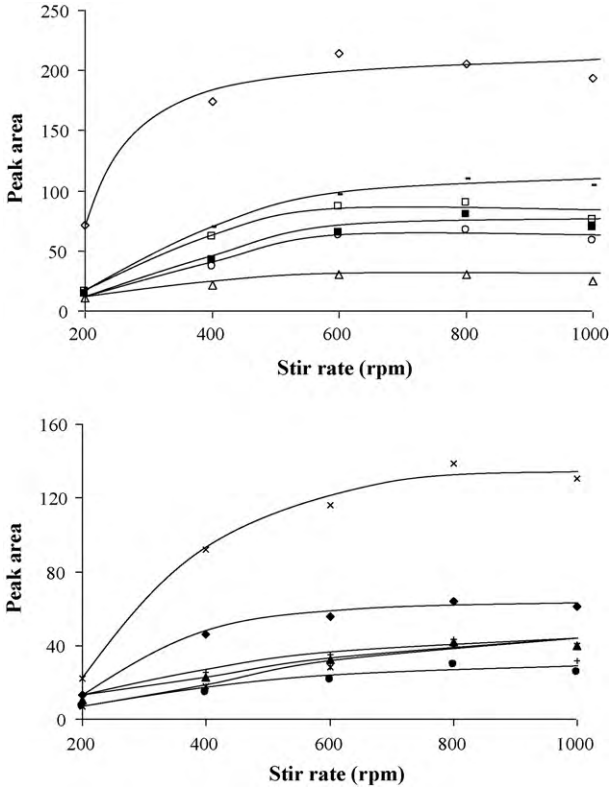

Fig. 3. Dependence of extraction peak area on stir rate using the poly(VBHDIm$^+$ NTf_2^-) PIL fiber. The extraction time was 30 min and the concentration of the analytes was: 1 μg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (◊), anthracene (–), and fluoranthene (x); 0.5 μg L^{-1} of pyrene (♦), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

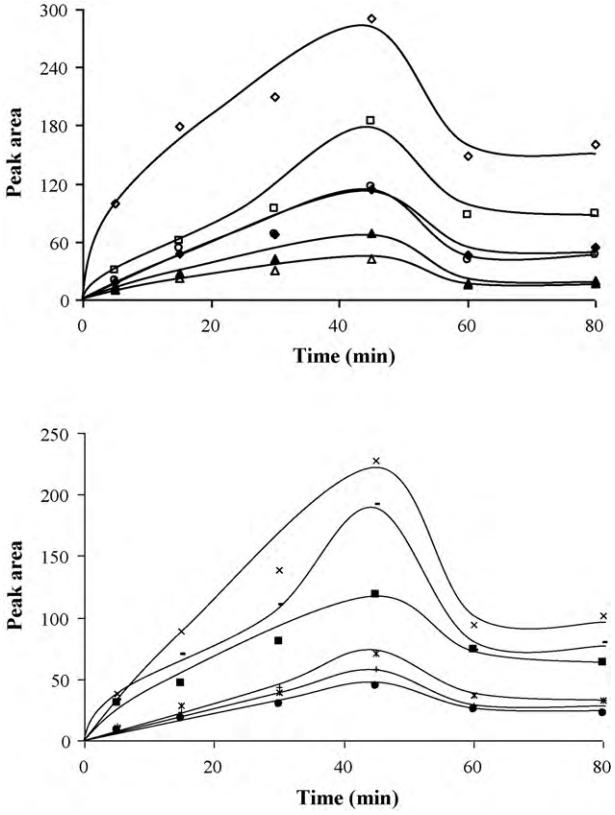

Fig. 4. Dependence of extraction peak area on extraction time using the poly(VBHDIm$^+$ NTf_2^-) PIL fiber. The stir rate was 800 rpm and the concentration of the analytes was: 1 μg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (◊), anthracene (–), and fluoranthene (x); 0.5 μg L^{-1} of pyrene (♦), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

analytes (1 and 0.5 μg L^{-1}) in the solution, the adsorption of the analytes to the wall of the sampling vial may be more pronounced for the poly(VBHDIm$^+$ NTf_2^-) PIL fiber compared to the poly(HDIm$^+$ NTf_2^-) PIL fiber in which the concentrations of the analytes was six-fold higher (6 and 3 μg L^{-1}). Compared with other studies using similar analytes [14,46], the more pronounced adsorption effect observed in our work may be due to the low concentration of analytes, the low content of the organic modifier (<1%) in extraction solution, the small sample volume (20 mL) and/or the relatively low extraction temperature (22 °C).

3.3. Extraction efficiency comparison of benzyl-functionalized PIL versus non-functionalized PIL and PDMS sorbent coatings

The extraction efficiencies of PAHs were examined by performing 30 min extractions at a stir rate of 800 rpm at room temperature using the two PIL and PDMS coatings. The extraction time of 30 min was chosen because at this time the PDMS fiber demonstrated the best performance for the extraction of the PAHs based on its sorption-time profiles (Fig. 6). A comparison of the amount of analyte extracted (in ng) for the three fibers using the same concentration of analytes is shown in Fig. 7. The PDMS fiber exhibited the lowest extraction efficiency for nearly all of the studied analytes compared to the two PIL fibers. The masses of acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene extracted by the two PIL fibers were between ten and fifty times higher than that obtained by the PDMS fiber. In the case of fluoranthene, pyrene, benzo(a)anthracene, and benzo(k)fluoranthene, the amount extracted varied between two and six times higher for the PIL-based fibers compared to PDMS while similar amounts of naphthalene and benzo(b)fluoranthene were extracted. Among the two PIL fibers, except for naphthalene, fluoranthene, and benzo(b)fluoranthene, where similar amounts of analyte were extracted, the poly(VBHDIm$^+$ NTf_2^-) PIL fiber exhibited superior extraction efficiency towards all PAHs. For acenaphthylene, acenaphthene, fluorene, pyrene, chrysene, and benzo(k)fluoranthene, the mass extracted by the poly(VBHDIm$^+$ NTf_2^-) PIL fiber was between 1.5 and 3 times higher than that obtained by the poly(HDIm$^+$ NTf_2^-) PIL fiber. In the case of benzo(a)anthracene, the poly(VBHDIm$^+$ NTf_2^-) PIL extracted nearly six times the mass extracted by the poly(HDIm$^+$ NTf_2^-) sorbent coating.

Calibration curves for all studied analytes were obtained for both PIL fibers and the PDMS fiber in deionized water. The figures of merit including linear ranges, correlation coefficients, sensitivities, and detection limits are listed in Tables 1–3. For the poly(VBHDIm$^+$ NTf_2^-) PIL fiber, the linear range was wide spanning from 2 to 4 orders of magnitude for many analytes with correlation coefficients varying between 0.981 and 0.999. Compared with the other two fibers, the poly(VBHDIm$^+$ NTf_2^-) PIL fiber generally exhibited wider linear ranges and better correlation coefficients for all studied PAHs. Limits of detection were calculated as three times the standard deviation of the lowest concentration divided by the slope of the calibration curve. Among the two PIL fibers, LODs for the poly(VBHDIm$^+$ NTf_2^-) PIL fiber were lower than the poly(HDIm$^+$ NTf_2^-) PIL fiber. LODs were in the range of 0.003–0.07 μg L^{-1} for the poly(VBHDIm$^+$ NTf_2^-) PIL fiber, 0.02–0.6 μg L^{-1} for the poly(HDIm$^+$ NTf_2^-) PIL fiber, and 0.1–6 μg L^{-1} for the PDMS fiber. In the case of naphthalene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo(k)fluoranthene, the obtained LODs were one order of mag-

Table 1
Figures of merit of calibration curves for 12 μm poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber[a].

Analyte	R	Calibration range (μg L^{-1})	Slope ± SD[b]	Error of the estimate[c]	LOD[d] (μg L^{-1})	%RSD[e]
Naphthalene	0.998	0.05–1000	14 ± 0.4	330	0.06	15
Acenaphthylene	0.997	0.005–1000	36 ± 1	929	0.01	10
Acenaphthene	0.992	0.05–1000	45 ± 2	1871	0.05	12
Fluorene	0.994	0.005–500	51 ± 2	1012	0.01	3
Phenanthrene	0.999	0.0125–100	50 ± 0.4	40	0.01	1
Anthracene	0.996	0.0125–100	37 ± 1	112	0.01	6
Fluoranthene	0.997	0.025–130	47 ± 1	167	0.02	8
Pyrene	0.997	0.01–9	71 ± 2	19	0.01	15
Benzo(a)anthracene	0.999	0.05–5	53 ± 2	9	0.03	6
Chrysene	0.995	0.003–5	452 ± 8	86	0.003	15
Benzo(b)fluoranthene	0.991	0.05–5	45 ± 3	16	0.05	13
Benzo(k)fluoranthene	0.981	0.05–9	8 ± 0.7	6	0.07	2

[a] Extraction conditions: sampling time, 45 min with stir rate of 800 rpm at 22 °C; desorption for 5 min at 250 °C; sample volume, 20 mL without headspace.
[b] Standard deviation of the slope.
[c] Standard deviation of the regression.
[d] Estimated as three times of standard deviation at the lowest concentration on the calibration curve divided by the slope of the calibration curve.
[e] Based on three extractions. The concentrations of the analytes were 1 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 0.5 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

Table 2
Figures of merit of calibration curves for 12 μm poly(HDIm$^+$ NTf$_2^-$) PIL fiber[a].

Analyte	R	Calibration range (μg L^{-1})	Slope ± SD[b]	Error of the estimate[c]	LOD[d] (μg L^{-1})	%RSD[e]
Naphthalene	0.986	0.5–1700	4 ± 0.2	390	0.6	11
Acenaphthylene	0.991	0.1–1700	17 ± 0.9	1457	0.2	7
Acenaphthene	0.989	0.1–1700	24 ± 1	2201	0.06	8
Fluorene	0.975	0.05–1700	27 ± 2	3586	0.02	9
Phenanthrene	0.988	0.05–130	30 ± 2	259	0.06	10
Anthracene	0.990	0.05–100	27 ± 2	156	0.05	15
Fluoranthene	0.987	0.025–100	27 ± 2	167	0.02	8
Pyrene	0.954	0.05–4	43 ± 6	22	0.06	12
Benzo(a)anthracene	0.965	0.1–5	12 ± 1	6	0.1	10
Chrysene	0.958	0.1–5	9 ± 1	6	0.2	8
Benzo(b)fluoranthene	0.968	0.5–5	8 ± 1	4	0.2	6
Benzo(k)fluoranthene	0.973	0.5–5	5 ± 0.6	2	0.3	15

[a] Extraction conditions: sampling time, 40 min with stir rate of 800 rpm at 22 °C; desorption for 5 min at 250 °C; sample volume, 20 mL without headspace.
[b] Standard deviation of the slope.
[c] Standard deviation of the regression.
[d] Estimated as three times of standard deviation at the lowest concentration on the calibration curve divided by the slope of the calibration curve.
[e] Based on three extractions. The concentrations of the analytes were 6 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 3 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

nitude lower for the poly(VBHDIm$^+$ NTf$_2^-$) PIL compared to the poly(HDIm$^+$ NTf$_2^-$) PIL. The LODs for chrysene were two orders of magnitude smaller using the same comparison. Sensitivities, as determined by the slopes of the calibration curves, were higher for all of the PAHs using the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber than those measured by the other two fibers.

Precision was determined by performing three consecutive extractions at a concentration of 1 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 0.5 μg L^{-1} for the remaining PAHs. In the case of the poly(VBHDIm$^+$ NTf$_2^-$) PIL fiber, the %RSD values varied between 1 and 15%. For the poly(HDIm$^+$ NTf$_2^-$) PIL and PDMS

Table 3
Figures of merit of calibration curves for 7 μm PDMS fiber[a].

Analyte	R	Calibration range (μg L^{-1})	Slope ± SD[b]	Error of the estimate[c]	LOD[d] (μg L^{-1})	%RSD[e]
naphthalene	0.984	6–500	0.08 ± 0.006	3	6	10
acenaphthylene	0.979	1–1700	0.6 ± 0.04	68	1	9
acenaphthene	0.981	1–1700	1 ± 0.09	142	1	10
fluorene	0.979	1–1700	1 ± 0.1	162	0.5	11
phenanthrene	0.990	1–100	1 ± 0.1	9	0.7	4
anthracene	0.972	1–100	2 ± 0.2	16	0.4	7
fluoranthene	0.994	0.5–100	6 ± 0.3	25	0.3	9
pyrene	0.971	0.1–8	30 ± 3	23	0.1	2
benzo(a)anthracene	0.972	0.1–8	10 ± 0.9	7	0.2	10
chrysene	0.971	0.1–5	15 ± 2	7	0.1	8
benzo(b)fluoranthene	0.991	0.5–4	27 ± 2	5	0.1	14
benzo(k)fluoranthene	0.946	0.5–8	2 ± 0.3	2	0.4	10

[a] Extraction conditions: sampling time, 30 min with stir rate of 800 rpm at 22 °C; desorption for 5 min at 250 °C; sample volume, 20 mL without headspace.
[b] Standard deviation of the slope.
[c] Standard deviation of the regression.
[d] Estimated as three times of standard deviation at the lowest concentration on the calibration curve divided by the slope of the calibration curve.
[e] Based on three extractions. The concentrations of the analytes were 6 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, and 3 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

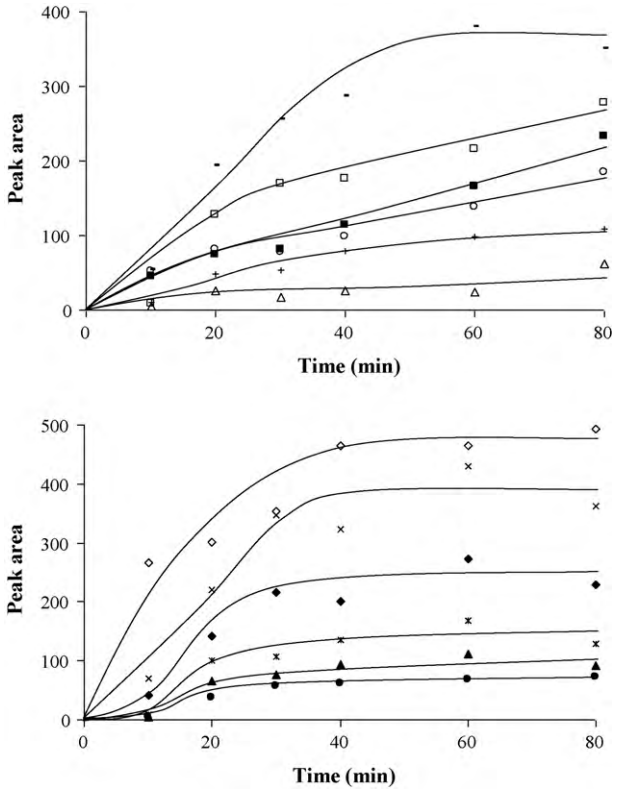

Fig. 5. Sorption-time profile of the poly(HDIm$^+$ NTf$_2^-$) PIL fiber. The stir rate was 800 rpm and the concentration of the analytes was: 6 μg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (◊), anthracene (–), and fluoranthene (x); 3 μg L^{-1} of pyrene (♦), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

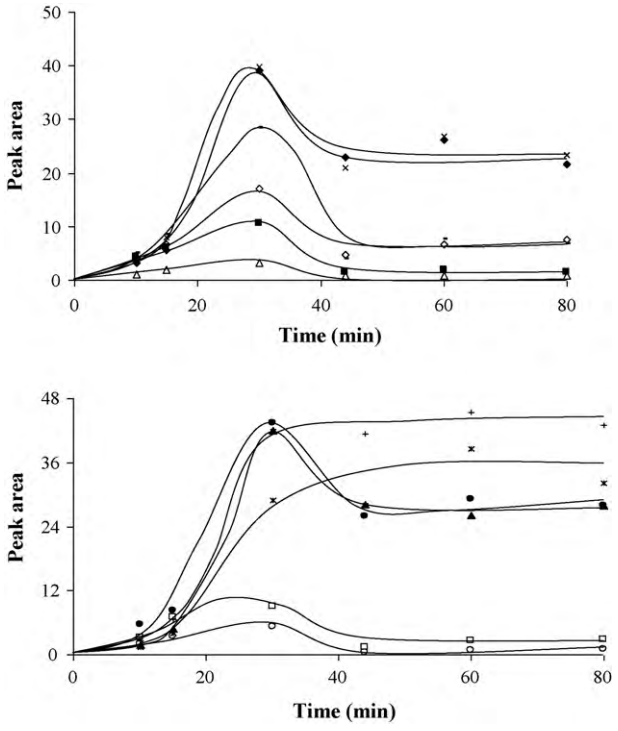

Fig. 6. Sorption-time profile of the PDMS (7 μm) fiber. The stir rate was 800 rpm and the concentration of the analytes was: 6 μg L^{-1} of naphthalene (△), acenaphthylene (○), acenaphthene (■), fluorene (□), phenanthrene (◊), anthracene (–), and fluoranthene (x); 3 μg L^{-1} of pyrene (♦), benzo(a)anthracene (*), chrysene (▲), benzo(b)fluoranthene (+), and benzo(k)fluoranthene (●).

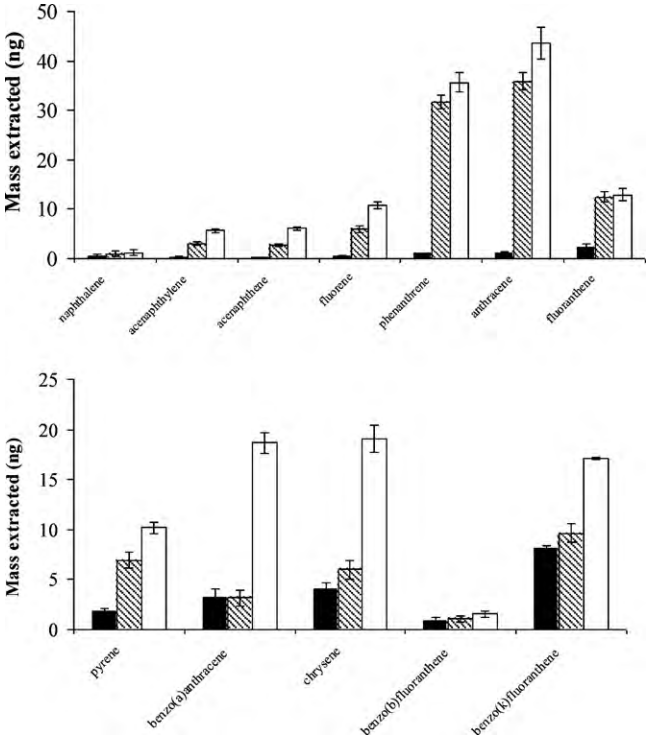

Fig. 7. Comparison of mass extracted using the three studied fibers: 7 μm PDMS (■), 12 μm poly(HDIm$^+$ NTf$_2^-$) (▨), and 12 μm poly(VBHDIm$^+$ NTf$_2^-$) (□). The extractions were performed for 30 min with a stir rate of 800 rpm at 22 °C. The concentration of the analytes was: 6 μg L^{-1} of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene; 3 μg L^{-1} of pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

fibers (examined at concentrations of 6 μg L^{-1} for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene; and 3 μg L^{-1} for pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene), %RSD values ranged from 6 to 15% and 2 to 14%, respectively.

Another meritorious feature of the poly(VBHDIm$^+$ NTf$_2^-$) PIL are the long lifetimes exhibited by the sorbent coating. Throughout the entire course of this study, one fiber was used with no significant loss of extraction efficiency up to approximately 70 extraction/desorption steps. The stability of the poly(VBHDIm$^+$ NTf$_2^-$) PIL sorbent coating was also examined by performing a series of 6-h extractions. For this PIL, the %RSD values ranged from 3 to 17% for three consecutive 6-h extractions.

3.4. Determination of PAH-PIL partition coefficients

In an effort to develop structure–function relationships to understand how analytes partition to PIL-based materials, partition coefficients were estimated using SPME. It is important to emphasize that the extraction time used in this study (i.e., 30 min) is shorter than the equilibrium time required by many of the PAHs; therefore, the partition coefficients determined in this study are only an estimate. The amount of analyte extracted by the fiber (n_f) was determined based on the linear relation of GC–FID response versus mass of analyte injected onto the chromatographic column. Partition coefficients ($\log K_{fs}$) for the two PILs and PDMS coatings are listed in Table 4. To ensure the accuracy of the methods used in this study, a comparison of literature $\log K_{fs}$ values for the same PAHs using 7 and 100 μm PDMS coatings are also included.

The partition coefficients of PAHs to the 7 μm PDMS coating are in reasonably good agreement with those reported in the lit-

Table 4
Estimated partition coefficients (K_{fs}) of PAHs to three different sorbent coatings.

Analyte	$\log K_{fs} \pm$ error				
	Poly(VBHDIm$^+$ NTf$_2^-$) (12 μm)	Poly(HDIm$^+$ NTf$_2^-$) (12 μm)	PDMS (7 μm)	PDMS (7 μm, literature)	PDMS (100 μm, literature)
Naphthalene	3.30 ± 0.16	3.34 ± 0.16	3.49 ± 0.29	2.73[c]	3.02,[a] 3.01,[b] 2.85[c]
Acenaphthylene	3.99 ± 0.07	3.87 ± 0.05	3.24 ± 0.27	na	3.40[a]
Acenaphthene	3.92 ± 0.06	3.93 ± 0.04	2.90 ± 0.16	na	3.63,[a]
Fluorene	4.26 ± 0.04	4.13 ± 0.02	3.44 ± 0.22	na	3.71,[a]
Phenanthrene	5.04 ± 0.11	4.67 ± 0.05	3.85 ± 0.05	4.42,[c] 3.25[d]	3.96,[a] 3.40,[c] 3.45[d]
Anthracene	4.85 ± 0.06	4.56 ± 0.07	3.90 ± 0.04	3.97,[c] 3.20[d]	3.98,[a] 4.10,[b] 3.14,[c] 3.46[d]
Fluoranthene	4.50 ± 0.07	4.20 ± 0.05	4.18 ± 0.10	4.38,[c] 3.72[d]	4.71,[a] 4.11,[c] 3.79[d]
Pyrene	4.57 ± 0.08	4.26 ± 0.07	4.38 ± 0.06	4.44,[c] 3.80[d]	4.86,[a] 4.07,[c] 3.82[d]

nd, not determined; na, not available.
[a] Ref. [46].
[b] Ref. [13].
[c] Ref. [47].
[d] Ref. [41].

erature, especially considering that some of the analytes are not under complete equilibrium. The larger errors in the obtained partition coefficients of naphthalene, acenaphthylene, acenaphthene, and fluorene can be ascribed to the low extraction peak areas (which are close to the detection limit of the method) for the 7 μm PDMS sorbent coating. Compared to the PAH-PDMS partition coefficients, the two PIL-based sorbent coatings exhibited larger $\log K_{fs}$ values for acenaphthene, acenaphthylene, fluorene, phenathrene, and anthracene. The results indicate a higher affinity of the PILs towards these PAHs. The impressive selectivity enhancement of the poly(VBHDIm$^+$ NTf$_2^-$) PIL over the PDMS sorbent coating can be observed by comparing the $\log K_{fs}$ values of acenaphthylene (3.99 versus 3.24), acenaphthene (3.92 versus 2.90), fluorene (4.26 versus 3.44), phenanthrene (5.04 versus 3.85), and anthracene (4.85 versus 3.90). A comparison of $\log K_{fs}$ values for the two PILs reveals that the poly(VBHDIm$^+$ NTf$_2^-$) PIL exhibits higher affinity towards all PAHs except for naphthalene and acenaphthene, in which similar $\log K_{fs}$ values were obtained.

4. Conclusions

The structural tuneability of polymeric ionic liquids was exploited in this study to design a new class of SPME sorbent coatings for the selective extraction of PAHs. The enhanced π–π interaction imparted to the sorbent coating, in addition to its ultra-hydrophobic nature, resulted in increased extraction selectivity of PAHs and long fiber lifetimes. Both of the PIL fibers demonstrated much higher extraction efficiencies towards the PAHs than the commercial PDMS fiber. This preliminary study provides, for the first time, an estimation of partition coefficients for 8 PAHs to PIL-based SPME coatings. The observed results clearly show that the benzyl-functionalized poly(VBHDIm$^+$ NTf$_2^-$) PIL exhibits higher extraction efficiency towards many of the PAHs compared to a similar PIL lacking such functionalization. This work demonstrates that by imparting specific functional groups into the structure of the PIL, the selectivity and extraction efficiency of the SPME sorbent coating can be effectively tuned and manipulated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.08.007.

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