



A novel aromatically functional polymeric ionic liquid as sorbent material for solid-phase microextraction

Juanjuan Feng^{a,b}, Min Sun^c, Jubai Li^a, Xia Liu^a, Shengxiang Jiang^{a,*}

^a Key Laboratory of Chemistry of Northwestern Plant Resources, CAS/Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100039, China

^c College of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

ARTICLE INFO

Article history:

Received 2 November 2011

Received in revised form 3 January 2012

Accepted 3 January 2012

Available online 10 January 2012

Keywords:

Polymeric ionic liquid

Solid-phase microextraction

Polycyclic aromatic hydrocarbons

Phthalate esters

Gas chromatography

ABSTRACT

Physical and chemical properties of ionic liquids (ILs) are significantly affected by types of their cations and anions. In this paper, a novel aromatically functional 1-vinyl-3-octylimidazolium 2-naphthalene-sulfonate salt was synthesized through metathesis reaction between 1-vinyl-3-octylimidazolium bromide and sodium 2-naphthalene-sulfonate, and polymerized onto the stainless steel wire *in situ* via surface radical chain-transfer reaction. Octanol/water distribution coefficient of the ionic liquid was studied and compared with that of 1-vinyl-3-octylimidazolium hexafluorophosphate. Partition coefficients of polycyclic aromatic hydrocarbons (PAHs) on these two polymeric ionic liquids-coated fibers indicated the enhanced hydrophobicity and aromaticity of the target IL. Analytical parameters exhibited high extraction efficiency of the novel fiber. Calibration ranges for several PAHs were from 0.02 to 200 $\mu\text{g L}^{-1}$. Limits of detection (LODs) were ranged from 0.005 to 0.01 $\mu\text{g L}^{-1}$. Application reliability of the proposed fiber was also investigated with some phthalate ester plasticizers. LODs were ranged from 0.02 to 0.05 $\mu\text{g L}^{-1}$. Hair spray and nail polish were used as real samples, and di-n-butyl phthalate and di-(2-ethyl-hexyl) phthalate were quantified with the established method.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Solid-phase microextraction (SPME) is popular in trace analysis due to its advantages such as absence of organic solvent, easiness to on-line coupling and high sensitivity. Since its first introduction by Pawliszyn and co-workers [1], SPME has gained increasing applications and tremendous developments. To date, almost all kinds of traditional and newfound materials have been used as coating materials for SPME fibers, such as some carbon nanostructured materials (carbon nanotubes [2–5], fullerenes [6], graphene [7,8], and porous carbon materials [9]), coinage metals [10,11], molecularly imprinted polymers [12–14], metal oxide [15–18], and commercially available organic polymers (polydimethylsiloxane (PDMS), polyacrylate (PA), carbowax/templated resin (CW-TPR), PDMS/divinylbenzene (PDMS-DVB), etc.).

Ionic liquids (ILs) are a broad class of salts which have organic cations (e.g. imidazolium, pyridinium, pyrrolidinium, tetraalkylphosphonium, alkylammonium) and inorganic (Cl^- , PF_6^- , BF_4^-) or organic anions (trifluoromethylsulfonate [CF_3SO_3^-],

bis[(trifluoromethyl)sulfonyl]imide [$(\text{CF}_3\text{SO}_2\text{N})^-$, trifluoroethanoate [CF_3CO_2^-], etc.). ILs are of interest because they have unique physicochemical properties, such as little measurable vapor pressure at room temperature, significant thermal stability and multiple solvation interactions with many types of organic, inorganic molecules or ions. ILs have made significant contributions to the development of analytical chemistry [19,20]. These have been reviewed respectively in liquid extraction of organic compounds [21], additives or support coating of capillary electrophoresis (CE) and electrochromatography (CEC) [19,22], stationary phases of gas chromatography (GC) [23], mobile phase modifier and surface-bonded stationary phase of high-performance liquid chromatography (HPLC) [24,25], sorbent materials of SPME [26], and so on.

One important feature of ILs is that varying the cation or anion may significantly affect their physical and chemical properties [20]. Combinations of variety of cations and anions give a tremendous number of ILs, from which they can be selected for specific applications. Anderson and co-workers [27,28] imparted polymeric ionic liquid (PIL) with aromatic character by functionalizing the cation with benzyl groups. The π - π interactions between aromatic analytes and the new PIL coating were enhanced greatly, and the extraction efficiencies were improved.

Anions have also been modified to tune properties of PILs. Lu et al. [29] designed a photosensitive material as liquid crystalline

* Corresponding author. Tel.: +86 931 4968266; fax: +86 931 8277088.
E-mail address: sxjiang@lzb.ac.cn (S. Jiang).

alignment layers constructed by coupling PIL with azobenzene dye methyl orange, as anion. Qiu et al. [30] used this method to tailor separation performance of a PIL-grafted silica stationary phase for HPLC. The stationary phase with methyl orange dye as counter anion exhibited ultra-high selectivity to polycyclic aromatic hydrocarbons (PAHs). Faul et al. [31] examined a class of multiple negatively charged azo-dyes complexed with a homologous series of cationic surfactants and found that the resulting dye–surfactant complexes formed highly organized supramolecular architectures, which were crystalline/liquid crystalline in nature. So pairwise ionic interactions [32] between individual cationic and anionic groups can be used as convenient and facile strategies to extend the structure properties of ionic liquids, and they can be achieved via metathesis reaction.

In this paper, properties of an imidazolium-based IL were tuned based on the reconstruction of its counter anion via metathesis reaction. The proposed IL was then polymerized *in situ* on stainless steel wire by surface radical chain-transfer reaction. Coupled to GC, extraction performance of the PIL-coated fiber was investigated with PAHs and phthalate ester (PAEs) as model analytes. Comparisons of extraction efficiency with other fibers were also performed. In addition, the established GC-SPME method was applied to determine several PAEs in two cosmetics products. The fiber showed acceptable extraction performance.

2. Experimental

2.1. Materials and reagents

The stainless steel wire was purchased from the Yixing Shenglong Metal Wire Net. Co. (Jiangsu, China). Naphthalene (Nap), fluorene (Flu), anthracene (Ant), fluoranthene (Flt) and chrysene (Chr) were obtained from the Shanghai Chemical Reagent Factory (Shanghai, China). Di-n-butyl phthalate (DBP), di-cyclohexyl phthalate (DCHP), di-(2-ethyl-hexyl) phthalate (DEHP), methanol, ethanol, chloroform, acetone and silver nitrate were purchased from the Tianjin Chemical Reagent Plant (Tianjing, China). Aqueous ammonia (NH₃·H₂O, 28 wt.%) was purchased from the Baiyin Liangyou Chemical Reagent Factory (Baiyin, China); glucose was purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 1,8-Octanedithiol was obtained from the Alfa Aesar (Ward Hill, MA, USA). Azodiisobutyronitrile (AIBN) was obtained from Shanpu Chemical Co. (Shanghai, China) and purified through recrystallization. 1-Vinyl-3-octylimidazolium bromide (VOIm⁺Br⁻) was purchased from Shanghai Chengjie Chemical Co. (Shanghai, China). Sodium-2-naphthalene-sulfonate was obtained from Aladdin reagent (Shanghai, China). Sulfuric acid (H₂SO₄, 98%) and nitric acid (HNO₃, 68%) were purchased from the Shanghai Chemical Reagent No. 1 Plant (Shanghai, China). All chemicals are

analytical reagents. Real samples of hair spray and nail polish were obtained from local market.

Stock solutions of PAHs and PAEs were prepared in ethanol at the concentrations of 0.2 mg mL⁻¹ and 1.0 mg mL⁻¹, respectively, and stored at 4 °C. Working solutions were prepared daily by diluting the stock solutions with water.

2.2. Apparatus

Analysis of the model compounds was performed with an Agilent 7890 GC system (Agilent Technologies, USA) equipped with a flame ionization detector (FID) and a split/splitless injector. The column used for the separation was HP-5 capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness).

Ultrapure nitrogen (>99.999%) was used as the carrier and make-up gas at 1 mL min⁻¹ and 25 mL min⁻¹, respectively. The injector was used in splitless mode at 250 °C. The detector temperature was fixed at 300 °C. Separation of PAHs was achieved using temperature programs as follows: the column temperature was initially held at 80 °C, and programmed at 25 °C min⁻¹ to 300 °C. For the separation of PAEs, the column temperature was programmed as follows: initial temperature was held at 150 °C and programmed at 10 °C min⁻¹ to 280 °C.

Evaluation of log *D* of the IL was performed on an Agilent 1100 Series modular HPLC system with a binary pump, a 20 μL sample loop and a UV–vis detector. Separations were carried out by a Hypersil ODS-2 column (250 mm × 4.6 mm i.d., 5 μm particle size) with methanol as mobile phase. Flow rate was 1 mL min⁻¹, and the optimum detection wavelength was fixed at 265 nm.

The vacuum drying oven DZG-6020 (SIMSUNG, Shanghai) was used to dry the target products before the characterization and preparation process.

Infrared (IR) spectrum instrument (Thermo Nicolet Nexus 870) and ¹H NMR (UNITY INOVA-400 MHz) were used to confirm the formation of VOIm⁺NapSO₃⁻. Surface properties of the proposed fiber were characterized by a scanning electron microscope (SEM, JSM-5600LV, JEOL Ltd., Japan).

2.3. Fiber preparation

2.3.1. Preparation of 1-vinyl-3-octylimidazolium 2-naphthalene-sulfonate

The preparation process of the novel PIL-coated fiber was described in Fig. 1. Two aqueous solutions of VOIm⁺Br⁻ and sodium-2-naphthalene-sulfonate with 1:1 charge ratio were mixed and stirred overnight at room temperature. After the reaction, the hydrophobic target IL was precipitated from the aqueous solution. Equal volume of chloroform was put into the aqueous mixture to extract IL. After demixing, the chloroform was separated and

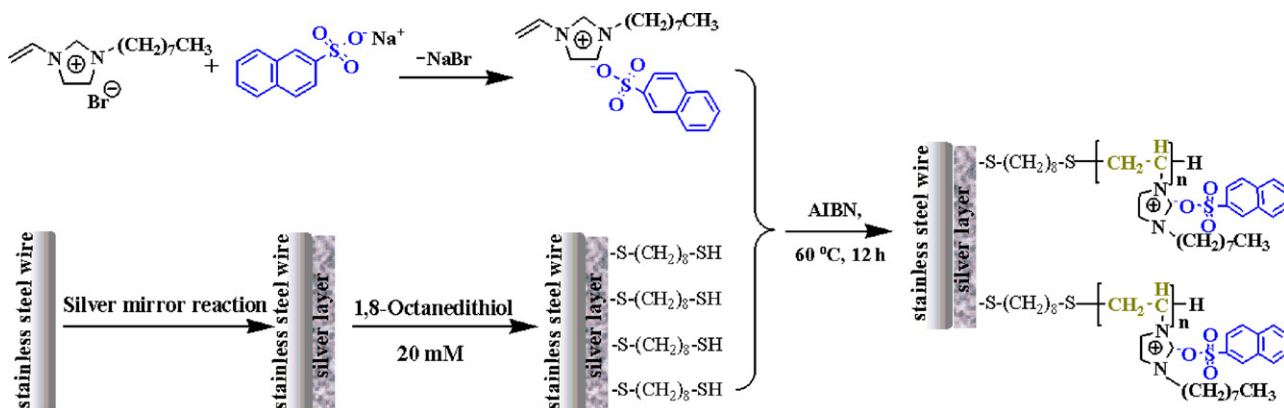


Fig. 1. Preparation schema of the poly(VOIm⁺NapSO₃⁻) coated fiber.

washed with fresh deionized water (1:1, v/v) several times to remove Br⁻ from the product until none Br⁻ was detected in the water phase. Then, chloroform was removed by vacuum distillation. The proposed IL was purified by recrystallization and dried in a vacuum.

¹H NMR of VOIm⁺NapSO₃⁻ (CD₃Cl, 400 MHz; δ, ppm, relative to TMS): δ 10.250–10.286 (d, 1H), 8.392 (s, 1H), 7.941–7.966 (d, 1H), 7.782–7.845 (m, 3H), 7.605 (s, 1H), 7.434–7.488 (m, 2H), 7.314–7.353 (m, 1H), 7.292 (s, 1H), 5.771–5.817 (m, 1H), 5.221–5.264 (m, 1H), 4.180–4.233 (m, 2H), 1.758 (m, 2H), 1.121–1.204 (m, 10H), 0.796–0.832 (t, 3H) (see Fig. S-1 in Supplementary materials).

2.3.2. Preparation of the PIL-coated SPME fiber

Two contiguous steps were involved in the preparation process of the novel PIL-coated fiber: functionalization of the stainless steel wire and the chain-transfer radical polymerization, which were described in detail in our previous studies [11,33]. Briefly, one end of the stainless steel wire (2 cm) was firstly washed with NaOH aqueous solution and then dipped in mixed acid (H₂SO₄:HNO₃=3:1, v/v) at 70 °C for several minute to remove the stable oxide on its surface. Then the fiber was washed with distilled water and dipped into the [Ag(NH₃)₂]⁺ solution to form microstructured silver layer by silver mirror reaction. After being dried at room temperature, the fiber was immersed in a solution of 1,8-octanedithiol in ethanol (20 mmol L⁻¹) for 24 h to form a self-assembled monolayer of dithiol. Then, the end of the thiol-functionalized fiber was immersed in 30 mL of chloroform solution containing 0.2 g of VOIm⁺NapSO₃⁻ and 0.0020 g of AIBN. After being purged for 10 min with nitrogen gas, the system was reacted at 60 °C for 12 h under nitrogen atmosphere. The IL was polymerized *in situ* on the surface of the stainless steel wire.

2.4. Solid-phase microextraction

All solid-phase microextractions were conducted in direct immersion mode with 10 mL working solution in a 15 mL vial. The fiber was installed into a homemade SPME device which was a modification of 5 μL syringe [34]. Before the experiment, it was aged at 250 °C for 15 min in the GC injector.

During the extraction, the aqueous samples were agitated with a magnetic stirring bar (1000 rpm). After the extraction, the analytes was desorbed in GC injector at 250 °C for 5 min. Possible carryover effect was removed by keeping the fiber in the injector for a second 5-min desorption.

The extraction of PAHs was performed under optimum extraction parameters: extraction time, 40 min; extraction temperature, 30 °C. The optimum extraction temperature for PAEs was 40 °C, and the extraction time was 30 min (see Figs. S-2–S-7 in Supplementary materials). Because of the ionic interaction between the cation and anion of PIL, working solutions for SPME was without salt to avoid possible metathesis reaction between the anion of PIL and halide anion of salt.

2.5. Hydrophobicity evaluations of VOIm⁺PF₆⁻ and VOIm⁺NapSO₃⁻

In order to investigate the hydrophobicity of the proposed IL, distribution coefficient (log *D*) was determined by the shake-flask method. 0.35 g of VOIm⁺PF₆⁻ and VOIm⁺NapSO₃⁻ were dissolved in 30 mL of 1-octanol/water (1:1, v/v) (1-octanol was pre-saturated with water before use), respectively. The solutions were stirred for 24 h and then kept still for 48 h to reach equilibrium at room temperature. Concentrations of the ILs in water phase were measured by HPLC with detection wavelength at 265 nm, and amount of IL

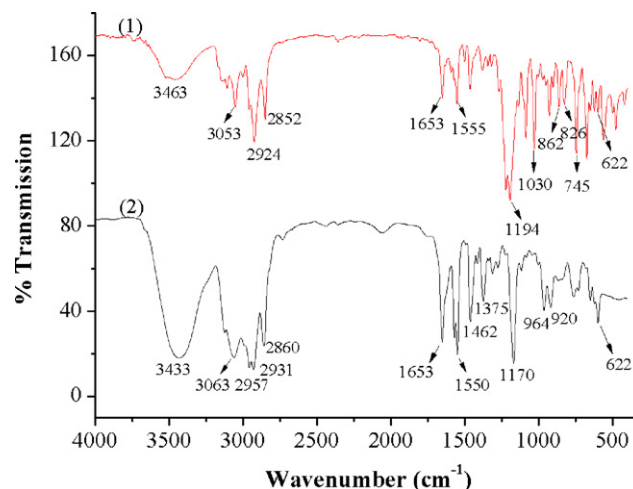


Fig. 2. FT-IR spectra of 1-vinyl-3-octylimidazolium 2-naphthalene-sulfonate (VOIm⁺NapSO₃⁻) (1) and 1-vinyl-3-octylimidazolium bromide (VOIm⁺Br⁻) (2).

in organic phase was calculated by difference of total and that in water. A series of standard solutions with methanol as solvent were prepared to make the standard curves for the quantification.

The log *D* values can be determined by Eq. (1):

$$\log D_{\text{oct/wat}} = \log \frac{[\text{IL}]_{\text{octanol}}}{[\text{IL}]_{\text{water}}^{\text{ionized}} + [\text{IL}]_{\text{water}}^{\text{neutral}}} \quad (1)$$

The log *D* is pH dependent, hence the pH at which the log *D* is measured must be specified. Of widely used is the log *D* at pH=7.4 (physiological pH of blood serum). So the pH values of the aqueous phases of VOIm⁺NapSO₃⁻ and VOIm⁺PF₆⁻ were both adjusted to 7.4 with phosphoric acid for the examinations.

VOIm⁺PF₆⁻ was obtained by the same procedure as reported in our previous work [33].

2.6. Preparation of real samples

1.0 g of hair spray was diluted to 100 mL with water in flask and kept at 4 °C for use. 1.0 g of nail polish was dissolved in 0.2 mL of ethanol and 99.8 mL of water. After a 10-min ultrasonic extraction, the solution was kept at 4 °C for use.

3. Results and discussion

3.1. Characterization of poly(VOIm⁺NapSO₃⁻)-coated fiber

The successful formation of aromatic IL is demonstrated by the appearance of IR bands in Fig. 2 (1) at 1194, 1030 cm⁻¹, corresponding to the antisymmetric and symmetric stretching vibrations of the sulfonic groups [29], and at 862, 826, 745 cm⁻¹, corresponding to the bending vibration of C–H of naphthyl. Bands around 1650 and 1550 cm⁻¹ in Fig. 2 (1) and (2) are attributed to the aromatic C=C or C=N stretching vibration, and at 651 cm⁻¹ is attributed to their bending vibration modes. Bands around 3050 cm⁻¹ are corresponding to the aromatic C–H stretching vibration. The other proof was provided by ¹H NMR spectra of VOIm⁺NapSO₃⁻ (see Supplementary material, Fig. S-1). The chemical shift of 8.392 (s, 1H), 7.941–7.966 (1H, d), 7.782–7.845 (3H, m) and 7.434–7.488 (2H, m) came from the proton signal of 2-naphthalenesulfonate (C₁₀H₇SO₃⁻). By comparison of the integral of the proton signal of IL with that of 2-naphthalenesulfonate, the ratio of integral areas is about 1:1, so it can be concluded that the stoichiometry of the cation and anion was equal to their charge ratio.

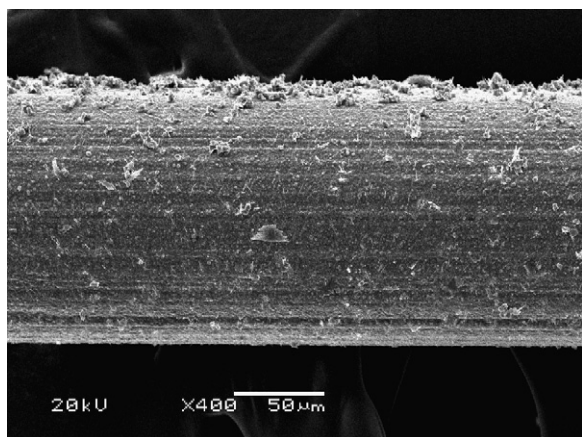


Fig. 3. SEM images of the poly(VOIm⁺NapSO₃⁻) coated fiber with magnification at 400 \times .

Log D_s of the proposed VOIm⁺NapSO₃⁻ and VOIm⁺PF₆⁻ were determined approximately by shake-flask method. Based on the experimental results, log D of VOIm⁺PF₆⁻ was 0.93, and log D of VOIm⁺NapSO₃⁻ was 1.25. So reconstruction of the counter anion with 2-naphthalene-sulfonate not only imparted aromaticity but also increased the hydrophobicity of IL. This was favorable for the extraction of some hydrophobic analytes.

Metathesis reaction was performed before polymerization in this work, which was different from other reports concerning the modification of anion of PIL [29–31]. Functionalization of anion before polymerization can guarantee the complete exchange of halide anion with NapSO₃⁻. Furthermore, remaining halide anion will decrease the thermal stability of PIL significantly [35,36].

Surface physical characteristic of the fiber was studied by SEM as shown in Fig. 3. Thickness of the PIL coating was about 5 μ m, which was much thinner than other PIL-coated fiber (12 μ m) prepared by several-times-dipping process [27,28].

3.2. Comparisons of extraction efficiency between poly(VOIm⁺NapSO₃⁻) and poly(VOIm⁺PF₆⁻) sorbent coatings for PAHs

The extraction property of the proposed poly(VOIm⁺NapSO₃⁻)-coated fiber was investigated and compared with poly(VOIm⁺PF₆⁻)-coated fiber based on the partition coefficients (K_{fs}) of PAHs. All the extraction procedures were performed under optimum conditions. Partition coefficients (K_{fs}) of the analytes between the coating material and aqueous solution were estimated according to Eq. (2) [37].

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

where n_0 is the initial amount of analyte in the sample solution, n_f is the amount of analyte on the fiber equilibrium, V_s is the sample volume, and V_f is the fiber coating volume. If the volume of the vial

is sufficiently large, the concentration change of the solute in the vial before and after SPME is negligible [38]. Eq. (2) can be changed as:

$$K_{fs} = \frac{V_s n_f}{V_f n_0} \quad (3)$$

In this work, the sample volume (V_s) was 10 mL; the initial amount of analytes (n_0) in the vial was 0.01 μ g; the n_f values, corresponding to the n_0 selected, was calculated by the calibration curves constructed by standard solution. Volume of the fiber coating (V_f) was calculated as 0.044 μ L. Because of the approximation of the V_f and n_f values, and the approximate equilibrium extraction for PAHs, the partition coefficients were only approximate.

As can be seen in Table 1, compared to the log K_{fs} of poly(VOIm⁺PF₆⁻) coating, the poly(VOIm⁺NapSO₃⁻) coating exhibits larger log K_{fs} for PAHs. Improvement of hydrophobicity and enhancement of π - π interactions based on the reconstruction of anion facilitated the high extraction capability. The partition coefficients of the model PAHs on poly(VBHDIm⁺NTf₂⁻) [27,28], cation of which was aromatically functionalized, were also included in Table 1. Values obtained in this work are lower than those reported in references but the changing trend with analytes from Nap to Chr is in acceptable agreement with them. We attributed the disparities to the inexact equilibrium during extraction. We also noted that the results presented in Refs. [27,28] using fibers with the same IL and comparable coating thickness produced similar but not identical results, suggesting differences in fiber bath-to-bath reproducibility.

3.3. Analytical performance for PAHs

Table 2 shows the analytical parameters of poly(VOIm⁺NapSO₃⁻)-coated fiber for the analysis of PAHs. Calibration ranges are obtained in the range of 0.05–200 μ g L⁻¹ for Nap, and 0.02–200 μ g L⁻¹ for Flu, Ant, Flt and Chr, with correlation coefficients (R) ranging from 0.991 to 0.999. Limits of detection (LODs) were calculated as three times the signal to noise ratio, and were investigated by extraction of aqueous samples spiked at different levels to meet such signal. LODs are 0.005 μ g L⁻¹ for Flt, and 0.01 μ g L⁻¹ for Nap, Flu, Ant and Chr. Repeatability of single fiber ranges from 4.37 to 11.7%, with five replication runs of working solution. Fiber-to-fiber repeatability with three fibers is ranged from 6.34 to 11.7%. Compared with the poly(VOIm⁺PF₆⁻)-coated fiber, slope of calibrations is larger, which means higher sensitivity for the model analytes. Analytical performance of the proposed poly(VOIm⁺NapSO₃⁻) coated fiber is comparable with that of the cationic functionalized PIL fiber [27].

3.4. Extended subsequent applications

To further investigate the application of poly(VOIm⁺NapSO₃⁻) coated fiber for other hydrophobic aromatic analytes, three PAEs were selected as the other series of model compounds. Table 3 includes the analytical performance of the fiber and other fibers. In this work, calibration ranges are from 0.1 to 200 μ g L⁻¹ for DBP

Table 1
Partition coefficients (K_{fs}) of PAHs obtained on proposed poly(VOIm⁺NapSO₃⁻) and poly(VOIm⁺PF₆⁻) coated fibers and literature values.

Compound	log K_{fs}			
	Poly(VOIm ⁺ NapSO ₃ ⁻)	Poly(VOIm ⁺ PF ₆ ⁻)	Poly(VBHDIm ⁺ NTf ₂ ⁻) [27]	Poly(VBHDIm ⁺ NTf ₂ ⁻) [28]
Nap	^a 2.82 \pm 0.12	^a 2.79 \pm 0.11	3.30 \pm 0.16	3.89–3.84
Flu	3.11 \pm 0.09	2.84 \pm 0.12	4.26 \pm 0.04	–
Ant	3.50 \pm 0.11	3.30 \pm 0.04	4.85 \pm 0.06	4.26–4.17
Flt	3.93 \pm 0.05	3.83 \pm 0.16	4.50 \pm 0.07	4.18–4.01
Chr	3.80 \pm 0.05	3.53 \pm 0.08	–	–

^a Average value \pm standard deviation ($N=3$).

Table 2
Analytical parameters of proposed poly(VOLm⁺NapSO₃⁻) fiber and comparisons with other PIL-coated fibers for the extraction of PAHs.

Compound	Poly(VOLm ⁺ NapSO ₃ ⁻)						Poly(VOLm ⁺ PF ₆ ⁻) [33]			Poly(VBHDIm ⁺ NTf ₂ ⁻) [27]	
	Calibration range (μg L ⁻¹)	R	^a Slope ± SD	LODs (μg L ⁻¹)	^b Single-fiber repeatability (n = 5, %)	^b Fiber-to-fiber repeatability (n = 3, %)	Calibration range (μg L ⁻¹)	Slope ± SD	LODs (μg L ⁻¹)	Calibration range (μg L ⁻¹)	LODs (μg L ⁻¹)
Nap	0.05–200	0.999	5.4 ± 0.5	0.01	11.7	6.89	–	–	–	0.05–1000	0.06
Flu	0.02–200	0.991	13.8 ± 2.4	0.01	5.57	11.7	0.05–500	19.0 ± 0.1	0.01	0.005–500	0.01
Ant	0.02–200	0.998	24.1 ± 2.9	0.01	4.37	7.42	0.05–200	15.0 ± 0.2	0.01	0.0125–100	0.01
Flt	0.02–200	0.996	50.5 ± 5.7	0.005	6.95	6.34	0.05–200	18.0 ± 0.2	0.01	0.025–130	0.02
Chr	0.02–200	0.994	30.0 ± 1.6	0.01	9.06	9.44	–	–	–	0.003–5	0.003

^a Calibration level: N = 7.

^b Standard addition level: 10 μg L⁻¹.

Table 3
Analytical parameters of poly(VOLm⁺NapSO₃⁻) coated fiber and comparisons with other fibers for the extraction of PAEs.

Compound	Poly(VOLm ⁺ NapSO ₃ ⁻)							Calix[6]arene [39]		Carbon nanotube/polypyrrole [40]	
	Calibration range (μg L ⁻¹)	R	log K _{fs}	^a Slope ± SD	LODs (μg L ⁻¹)	^b Single-fiber repeatability (n = 5, %)	^b Fiber-to-fiber repeatability (n = 3, %)	Calibration range (μg L ⁻¹)	LODs (μg L ⁻¹)	Calibration range (μg L ⁻¹)	LODs (μg L ⁻¹)
DBP	0.1–200	0.998	2.67 ± 0.03	3.86 ± 0.20	0.05	4.83	12.9	1.6–1600	0.064	0.5–300	0.07
DCHP	0.05–200	0.999	3.71 ± 0.14	14.2 ± 2.1	0.02	7.66	6.68	0.48–480	0.008	–	–
DEHP	0.05–200	0.998	3.85 ± 0.08	24.7 ± 0.6	0.02	7.67	7.18	–	–	–	–

^a Calibration level: N = 7.

^b Standard addition level: 10 μg L⁻¹.

and 0.05 to 200 μg L⁻¹ for DCHP and DEHP, with high correlation coefficients from 0.998 to 0.999. The partition coefficients of PAEs were also estimated and the values are from 2.67 to 3.85. LODs are ranged from 0.02 to 0.05 μg L⁻¹. Single fiber repeatability and fiber-to-fiber repeatability are both in acceptable ranges. Compared with calix[6]arene [39] and carbon nanotube/polypyrrole [40] coated SPME fibers, LODs and lowest point of calibration ranges are of the same order.

3.5. Application to real samples

Hair spray and nail polish were collected from local market and used as real samples in this work. Organic additives and solvents especially those with high concentrations in hair spray had much influence on extraction recoveries. For the accurate quantification of proposed analytes, a standard addition method was employed to compensate the matrix effect. Addition levels were at 5, 20, 40, and 60 μg L⁻¹ in solution of hair spray, and 5, 20, 30, and 40 μg L⁻¹ in solution of nail polish, respectively. Three replicates were performed for each standard addition level, and the average values of the replicates were the final data for standard curves. The determination result is included in Table 4. GC-FID chromatograms of the real samples with and without standard addition are shown in Figs. 4 and 5. DBP and DEHP are quantified with concentration at 0.46 and 0.30 μg g⁻¹ in hair spray. DEHP in nail polish is calculated at 1.74 μg g⁻¹. From these results it can be concluded that the proposed fiber has general application to hydrophobic aromatic compounds.

Table 4
Determinations of three PAEs in hair spray and nail polish.

Compound	Hair spray			Nail polish		
	^a Calibration curve	R	Concentration (μg g ⁻¹)	^a Calibration curve	R	Concentration (μg g ⁻¹)
DBP	Y = (2.77 ± 0.06)X + (12.6 ± 0.3)	0.9995	0.46 ± 0.02	–	–	–
DCHP	–	–	–	–	–	–
DEHP	Y = (3.49 ± 0.07)X + (10.0 ± 0.4)	0.9994	0.30 ± 0.03	Y = (18.2 ± 0.4)X + (317 ± 14)	0.9997	1.74 ± 0.11

^a Obtained from the standard addition method.

^b Standard error.

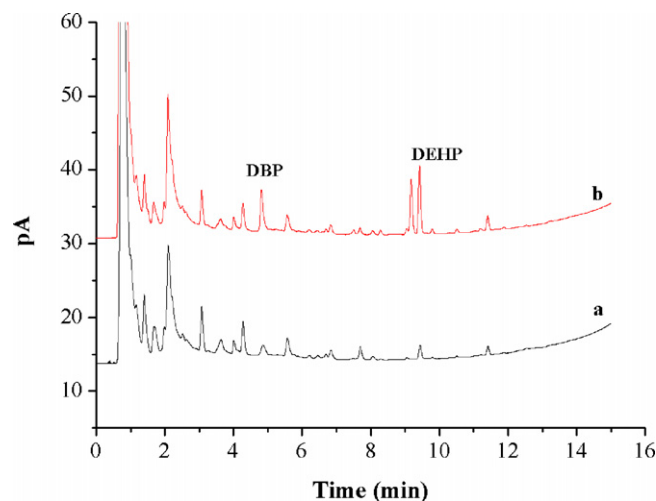


Fig. 4. GC-FID chromatograms of hair spray solution obtained by SPME. Standard addition level: 0 μg L⁻¹ (a) and 60 μg L⁻¹ (b).

3.6. Durability and fiber lifetime

Most of PILs possess high thermal stability. Thermal decomposition temperatures were observed at the range of 350 °C to >400 °C [26]. But when SPME is coupled to GC, viscosity of PILs often decreases at elevated temperature, which leads to the thermal bleeding of PILs. The *in situ* polymerization of ionic liquid on the

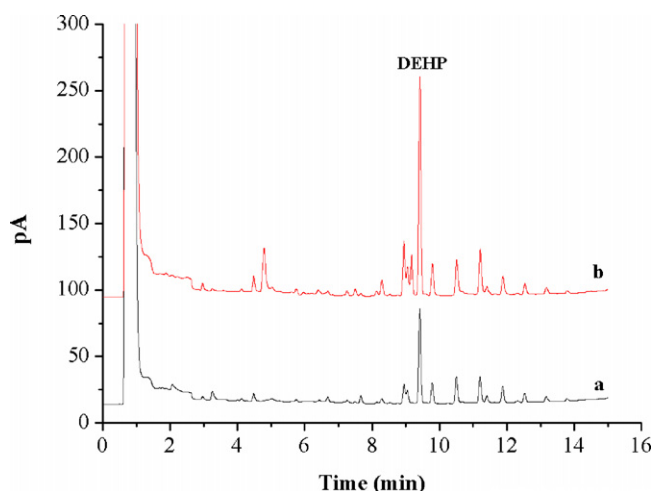


Fig. 5. GC-FID chromatograms of nail polish solution obtained by SPME. Standard addition level: $0 \mu\text{g L}^{-1}$ (a) and $40 \mu\text{g L}^{-1}$ (b).

surface of supporting substrate was focused on the improvement of stability and durability of PIL coated fiber [33]. In this work, the PIL-coated fiber was firstly aged at 250°C before extraction process, with the aim of removing the IL monomers or polymers with lower polymerization degree physically adsorbed onto the fiber. The fiber can be used over one hundred times without obvious decrease in extraction efficiency. While higher desorption temperature brought more obvious bleeding, and the fiber lifetime would be greatly reduced.

4. Conclusions

In this paper, properties of ionic liquid were simply tuned based on the modification of its anion via metathesis reaction. The proposed IL, with 2-naphthalene-sulfonate as building anion unit, exhibited enhanced hydrophobicity and aromaticity based on the studies of its octanol/water distribution coefficient and partition coefficients of PAHs. Extended subsequent application was investigated with PAEs as model analytes. High extraction efficiency was also obtained. Hair spray and nail polish were used as real samples and some PAEs were quantified in them. Performance of the proposed fiber indicated that modification of anions was another efficient process to impart special functionalizations to ILs.

Acknowledgments

The authors would like to thank the National Science Foundation of China for the financial support of this research (Nos. 20975105, 201105107 and 201175143).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.01.010.

References

- [1] R.P. Belardi, J. Pawliszyn, *Water Pollut. Res. J. Can.* 24 (1989) 179.
- [2] X.Y. Liu, Y.S. Ji, Y.H. Zhang, H.X. Zhang, M.C. Liu, *J. Chromatogr. A* 1165 (2007) 10.
- [3] R.F. Jiang, F. Zhu, T.G. Luan, Y.X. Tong, H. Liu, G.F. Ouyang, J. Pawliszyn, *J. Chromatogr. A* 1216 (2009) 1305.
- [4] N. Rastkari, R. Ahmadkhanlari, M. Yunesian, *J. Chromatogr. B* 877 (2009) 1568.
- [5] J.J. Feng, M. Sun, L.L. Xu, J.B. Li, X. Liu, S.X. Jiang, *J. Sep. Sci.* 34 (2011) 2482.
- [6] C.H. Xiao, S.Q. Han, Z.Y. Wang, J. Xiang, C.Y. Wu, *J. Chromatogr. A* 927 (2001) 121.
- [7] J.M. Chen, J. Zou, J.B. Zeng, X.H. Song, J.J. Ji, Y.R. Wang, J. Ha, X. Chen, *Anal. Chim. Acta* 678 (2010) 44.
- [8] H. Zhang, H.K. Lee, *J. Chromatogr. A* 1218 (2011) 4509.
- [9] F. Zhu, J.M. Guo, F. Zeng, R.W. Fu, D.C. Wu, T.G. Luan, Y.X. Tong, T.B. Lu, G.F. Ouyang, *J. Chromatogr. A* 1217 (2010) 7848.
- [10] J.J. Feng, M. Sun, H.M. Liu, J.B. Li, X. Liu, S.X. Jiang, *J. Chromatogr. A* 1217 (2010) 8079.
- [11] J.J. Feng, M. Sun, J.B. Li, X. Liu, S.X. Jiang, *Anal. Chim. Acta* 701 (2011) 174.
- [12] F.G. Tamayo, E. Turiel, A. Martín-Esteban, *J. Chromatogr. A* 1152 (2007) 32.
- [13] B.B. Prasad, M.P. Tiwari, R. Madhuri, P.S. Sharma, *J. Chromatogr. A* 1217 (2010) 4255.
- [14] E. Turiel, A. Martín-Esteban, *J. Sep. Sci.* 32 (2009) 3278.
- [15] D. Djozan, Y. Assadi, S.H. Haddadi, *Anal. Chem.* 73 (2001) 4054.
- [16] H.M. Liu, D.A. Wang, L. Ji, J.B. Li, S.J. Liu, X. Liu, S.X. Jiang, *J. Chromatogr. A* 1217 (2010) 1898.
- [17] A. Mehdinia, M.F. Mousavi, M. Shamsipur, *J. Chromatogr. A* 1134 (2006) 24.
- [18] H.L. Xu, Y. Li, D.Q. Jiang, X.P. Yan, *Anal. Chem.* 79 (2007) 6903.
- [19] S.A. Shamsi, N.D. Danielson, *J. Sep. Sci.* 30 (2007) 1729.
- [20] P. Sun, D.W. Armstrong, *Anal. Chim. Acta* 661 (2010) 1.
- [21] C.F. Poole, S.K. Poole, *J. Chromatogr. A* 1217 (2010) 2268.
- [22] M. López-Pastor, B.M. Simonet, B. Lendl, M. Valcárcel, *Electrophoresis* 29 (2008) 94.
- [23] C. Yao, J.L. Anderson, *J. Chromatogr. A* 1216 (2009) 1658.
- [24] Y. Polyakova, Y.M. Koo, K.H. Row, *Biotechnol. Bioprocess Eng.* 11 (2006) 1.
- [25] Y. Wang, M.L. Tian, W.T. Bi, K.H. Row, *Int. J. Mol. Sci.* 10 (2009) 2591.
- [26] T.D. Ho, A.J. Canestraro, J.L. Anderson, *Anal. Chim. Acta* 695 (2011) 18.
- [27] Y.J. Meng, J.L. Anderson, *J. Chromatogr. A* 1217 (2010) 6143.
- [28] J. López-Darias, V. Pino, Y.J. Meng, J.L. Anderson, A.M. Afonso, *J. Chromatogr. A* 1217 (2010) 7189.
- [29] S.F. Xiao, X.M. Lu, Q.H. Lu, *Macromolecules* 40 (2007) 7944.
- [30] H.D. Qiu, M. Takafuji, T. Sawada, X. Liu, S.X. Jiang, H. Ihara, *Chem. Commun.* 46 (2010) 8740.
- [31] Y. Guan, M. Antonietti, C.F.J. Faul, *Langmuir* 18 (2002) 5939.
- [32] C.F.J. Faul, M. Antonietti, *Adv. Mater.* 15 (2003) 673.
- [33] J.J. Feng, M. Sun, L.L. Xu, J.B. Li, X. Liu, S.X. Jiang, *J. Chromatogr. A* 1218 (2011) 7758.
- [34] J.F. Liu, N. Li, G.B. Jiang, J.M. Liu, J.Å. Jönsson, M.J. Wen, *J. Chromatogr. A* 1066 (2005) 27.
- [35] J.L. Anderson, D.W. Armstrong, *Anal. Chem.* 75 (2003) 4851.
- [36] Q.C. Zhao, J.L. Anderson, *J. Sep. Sci.* 33 (2010) 79.
- [37] J. Pawliszyn, *Solid-Phase Microextraction: Theory and Practice*, Wiley-VCH, Chichester, 1997.
- [38] R.F. Jiang, F. Zhu, T.G. Luan, Y.X. Tong, H. Liu, G.F. Ouyang, J. Pawliszyn, *J. Chromatogr. A* 1216 (2009) 4641.
- [39] C.W. Ye, J. Gao, C. Yang, X.J. Liu, X.J. Li, S.Y. Pan, *Anal. Chim. Acta* 641 (2009) 64.
- [40] H. Asadollahzadeh, E. Noroozian, S. Maghsoudi, *Anal. Chim. Acta* 669 (2010) 32.