



Preparation and characterization of novel crown ether functionalized ionic liquid-based solid-phase microextraction coatings by sol-gel technology

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ABSTRACT

A novel crown ether functionalized ionic liquid (IL), 1-allyl-3-(6'-oxo-benzo-15-crown-5 hexyl) imidazolium hexafluorophosphate was synthesized and used as selective stationary phase to prepare task-specific IL-based solid phase microextraction (SPME) fibers by sol-gel method and free radical cross-linking technology. The underlying mechanism of the sol-gel reaction was proposed and the successful chemical bonding of the crown ether functionalized IL to the formed hybrid organic-inorganic copolymer coating was confirmed by FT-IR spectroscopy. The performance of this in situ created crown ether functionalized IL-based SPME fibers, was investigated in detail. The coating has porous surface structure, stable performance in high temperature (to 340 °C) and in different solutions (water, organic solvent, acid and alkali), and good coating preparation reproducibility. In contrast to the sol-gel derived 1-allyl-3-methyl imidazolium hexafluorophosphate-based coating prepared in our previous work with the identical procedure, the extraction performance of this newly developed sol-gel crown ether functionalized IL-based coating was superior for alcohols, phthalate esters, phenolic environmental estrogens, fatty acids and aromatic amines due to the introduction of benzo-15-crown-5 functional group in IL structure. Moreover, it was shown to provide higher or comparable extraction efficiencies for most analytes studied than did the commercial PDMS, PDMS/DVB and PA fibers.

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1. Introduction

Solid-phase microextraction (SPME), introduced by Pawliszyn, is a fast, solvent-free alternative to conventional sample extraction techniques [1]. The key part of the SPME technique is the sorbent coating immobilized on the fiber substrate. Therefore, the preparation of highly selective, stable and effective sorbent coatings will be one of the most important aspects of future developments in SPME technology [2,3].

Ionic liquids (ILs) are a new class of non-molecular solvents consisting entirely of ionic components, an organic cation and either an organic or an inorganic anion [4]. They have many fascinating properties including: wide liquid ranges, negligible vapor pressure, high thermal and chemical stability, good film-forming ability, strong polarity and good solvating properties, wide range of viscosities, high electrolytic conductivity, reusability and non-flammability [5]. However, the most important feature of ILs is that their physical and chemical properties can be tuned by varying or introducing

new substitutive group in the cation or the combined anion. Owing to these unique characteristics, ILs have received intensive attention in analytical chemistry, especially in separation science over the past few years [6,7].

Considering that ILs can serve not only as selective stationary phase [8,9] but also as desirable extraction medium [10–12], they can be favorable candidates for SPME coating materials [13–20]. The preparation and application of IL-coated fibers for SPME was first introduced by Liu and co-workers [13], followed by Hsieh et al. [14], who reported the development of Nafion membrane-supported IL coating for analyzing polycyclic aromatic hydrocarbons (PAHs) in water samples. Both of these two fibers were coated with a disposable IL-based coating, which need to be washed away by organic solvents after each use and recoated before the next extraction. To obtain reusable IL-based SPME fibers, polymeric IL-based coatings were developed and applied to extract esters [15], amphetamine metabolite [16] and PAHs [17], etc. Very recently, SPME fibers based on polymeric IL-bonded silica particles were developed and used for extracting a large variety of polar solutes with headspace and direct-immersion modes [18]. The stability, mechanical strength and durability were improved accordingly, owing to the chemical binding between the polymeric ILs and silica particles.

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Sol-gel technology provides a simple, convenient and reliable method for the preparation of SPME fibers through in situ creation of surface-bonded organic-inorganic hybrid coatings on the outer surface of the fused-silica fibers or the inner surface of the capillaries [21,22]. To obtain desirable chemical and thermal stability, strong polarity and tailored porosity, coating materials with special structure and function should be introduced to the sol solution. Owing to their specific molecular structure, ILs have been used as excellent solvents and pore templates to prepare various hybrid organic-inorganic coatings for SPME and capillary microextraction by sol-gel technology [23,24]. After the fibers and capillaries were coated with the sol-gel polymers, they were then thermally conditioned above the decomposition temperatures of ILs used and then rinsed with organic solvents. Therefore, ILs did not participate in the extraction process since they had been removed from the sol-gel coatings prior to use. The higher extraction performance of these IL-mediated sol-gel coatings was mainly attributed to their more porous morphology in comparison with the analogous sol-gel coatings prepared without ILs. However, IL-generated porous surface structure alone is not enough to provide desired extraction efficiency. To make full use of both the template and the sorbent functions of ILs, two allyl-functionalized ILs were used as selective stationary phase to prepare chemically bonded IL-based organic-inorganic hybrid SPME fibers with the aid of γ -methacryloxypropyltrimethoxysilane (KH-570) as bridge by sol-gel method and free radical crosslinking technology in our previous work [25]. Thanks to the strong chemical binding between ILs and the formed silica substrate, ILs introduced can be retained in coating during the thermal and solvent desorption, leading to high selectivity and sensitivity towards strong polar phenolic environmental estrogens (PEEs) and aromatic amines.

Crown ether is a class of macrocyclic polyether compound whose structure contains 4–20 oxygen. The cavity structure and the strong electronegative effect of heteroatoms on the crown ether ring result in good selectivity as chromatographic stationary phases [26,27]. The first use of crown ether as coating materials for SPME was reported by Zeng et al. in 2001 [28]. These coatings had stable performance in high temperature (up to 350 °C) and possessed unique selectivity for phenolic compounds. Subsequent researches indicated that crown ether-based SPME coatings also had excellent selectivity for other polar compounds, such as organophosphorus pesticides [29], biogenic amines [30] and aromatic amines [31].

In this work, a novel IL 1-allyl-3-(6'-oxo-benzo-15-crown-5 hexyl) imidazolium hexafluorophosphate ([A(Benzo15C5)HIM][PF₆]) was synthesized and used as selective stationary phase for SPME in order to take full advantage of the unique properties of both IL and benzo crown ether. Owing to the introduction of allyl substituent in the tag end, this crown ether functionalized IL-based SPME fiber can be prepared with the aid of KH-570 as bridge using sol-gel method and free radical crosslinking technology. Its surface morphology, thermal and chemical stability, selectivity and extraction efficiency were compared with the 1-allyl-3-methyl imidazolium hexafluorophosphate ([AMIM][PF₆])-based fiber prepared in our previous work with an identical preparation procedure [25], to validate the effect of benzo-15-crown-5 functional group on the performance of crown ether functionalized IL-based SPME fiber.

2. Materials and methods

2.1. Apparatus

A magnetic stirrer DF-101B (Zhengzhou Greatwall Scientific Industrial and Trading Co., Ltd., Zhengzhou, China) was used for stirring the sample during extraction. A centrifuge model Neofuge-

23R (Heal Force Development Co., Ltd., Shanghai, China) was used to separate the sol solution from the precipitate. To mix various solution ingredients thoroughly, an ultrasonicator model SB-3200 (Branson Ultrasonics Co., Ltd., Shanghai, China) was used. A SP-6890 capillary GC system (Shandong Lunan Ruihong Chemical Instrument Corporation, Shandong, China) equipped with a capillary split/splitless injector and flame ionization detector (FID) was employed for assessing the performance of the developed crown ether functionalized IL-based sol-gel SPME fibers. On-line data collection and processing were accomplished on N2000 Chromastation Software (Zhejiang University Zhida Information Engineering Co., Ltd., Hangzhou, China). The chromatography separations were performed using a SE-54 fused silica capillary column (30 m × 0.25 mm I.D., 0.25 μ m film thickness) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China) and a Cp-sil 88 fused silica capillary column (30 m × 0.25 mm I.D., 0.2 μ m film thickness) (Varian, Walnut Creek, CA, USA). A ZF-1 Type Ultraviolet Analysis Instrument for Three Purposed (Shanghai Jinpeng Analytical Instruments Co., Ltd., Shanghai, China) was used for the free radical cross-linking copolymerization of crown ether functionalized IL and the silane coupling agent as precursor. Infrared spectra were recorded using IR instrument model FTIR-8201PC (Shimadzu, Kyoto, Japan). A Perkin-Elmer TGA-2 Thermogravimetric Analyzer was used to evaluate the thermal stability of the developed sol-gel crown ether functionalized IL-based SPME coatings (Netzsch, Selb, Germany). The analysis of the surface morphology characteristics of the coated fibers was performed with a Hitachi X-650 scanning electron microscope (Hitachi, Tokyo, Japan). The fused-silica fibers (125 μ m, O.D.) with protective polyimide coating were provided by Fiberhome Telecommunication Technologies Co., Ltd., Wuhan, China. Homemade SPME syringes with sol-gel-derived [A(Benzo15C5)HIM][PF₆]-based fibers and [AMIM][PF₆]-based fibers were used in this work. The commercial PDMS (100 μ m), PDMS/DVB (65 μ m) and PA (85 μ m) coated fibers were purchased from Supelco (Bellefonte, PA, USA).

2.2. Reagents and materials

[AMIM][PF₆] was purchased from Chengjie Chemical Co., Ltd., Shanghai, China. Hydroxy-terminated silicone (OH-TSO) and poly (methylhydrosiloxane) (PMHS) were obtained from Xinli Chemical Industry Co., Ltd., Zigong, China. Tetraethoxysilane (TEOS) and KH-570 were purchased from the Chemical Plant of Wuhan University (Wuhan, China). Trifluoroacetic acid (TFA) and benzophenone were obtained from Aladdin Reagent Co., Ltd., Shanghai, China. 4-Tert-butylphenol (4-TBP), 4-tert-octylphenol (4-TOP), bisphenol A (BPA), 2,4,6-trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP), aniline(A), o-toluidine(OT), 2,4-dimethylaniline(2,4-DMA), 3,4-dimethylaniline(3,4-DMA) and N,N-diethyl-aniline(2-EA) were purchased from Aladdin Reagent Co., Ltd., Shanghai, China. Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diamyl phthalate (DAP), diisooctyl phthalate (DIOP), di-n-octyl phthalate (DnOP), dinonyl phthalate (DNP), didecyl phthalate(DDP), 1-propanol, isobutyl alcohol, 1-butyl alcohol, isoamyl alcohol, 1-amyl alcohol, 1-hexanol, 1-octanol, isobutyric acid, valeric acid, hexanoic acid, heptanoic acid, octanoic acid, NaCl, CH₂Cl₂, CH₃OH, acetone and acetonitrile were of analytical-reagent grade and supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.3. Synthesis of [A(Benzo15C5)HIM][PF₆]

The [A(Benzo15C5)HIM][PF₆] was synthesized according to the procedure depicted in Fig. 1.

Synthesis of dichlorotetraglycol: 0.252 mol tetraethylene glycol, 100 mL benzene, and 45 mL pyridine were successively added to

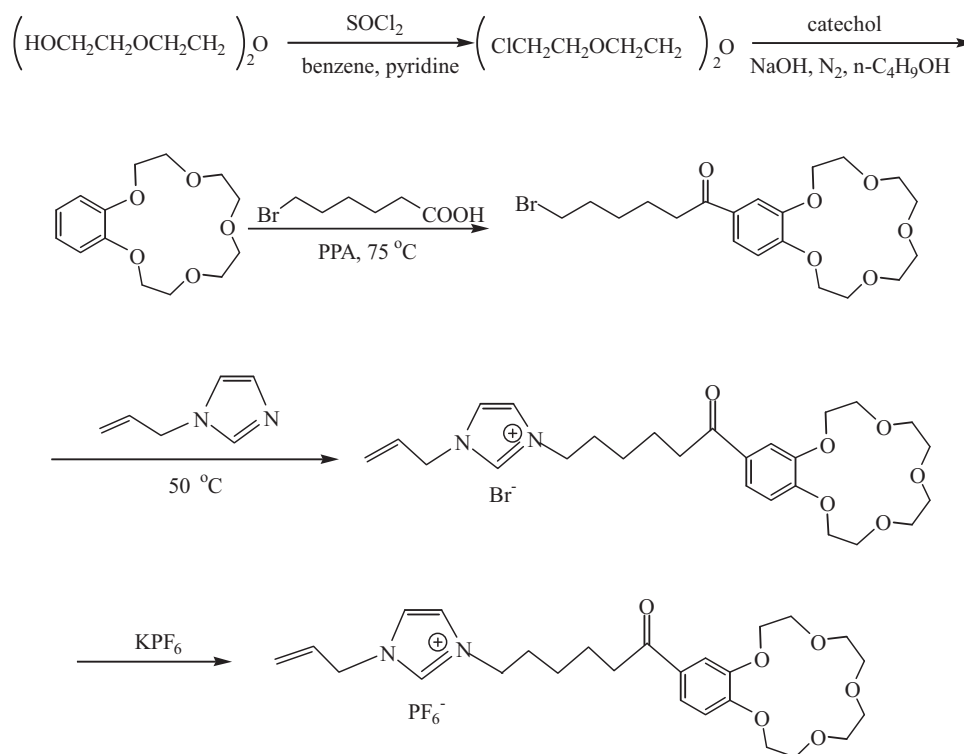


Fig. 1. Synthetic route of [A(Benzo15C5)HIM][PF₆].

a 500-mL 3-mouth flask. The mixture was stirred under reflux at 86 °C for 1 h. Then 45 mL thionyl chloride was added to this mixture. After 18 h of stirring under reflux at 86 °C, the mixture was cooled to room temperature, and acidized with 35 mL 3 mol L⁻¹ of HCl solution. All of them were transferred to the separatory funnel for separation. The upper layer liquid was washed with saturated sodium carbonate until the liquid became neutral. The solvent was recovered via rotary evaporation and dried with anhydrous magnesium sulfate. After the removal of the desiccant, the products were refluxed in the presence of activated carbon, and filtrated under reduced pressure. 45.01 g of dichlorotetraethylene glycol was obtained with the yield of 77.67%.

Synthesis of benzo-15-crown-5: 21 mL NaOH solution was added to a 500-mL 3-mouth flask containing 274 mL *n*-C₄H₉OH under the nitrogen atmosphere. After stirring for 10 min, 20.51 g of *o*-dihydroxybenzene was added. This mixture was heated to 102 °C and stirred for another 30 min. Then a one to one mole ratio of dichlorotetraethylene glycol to *o*-dihydroxybenzene was slowly added into the mixture. The reactant was stirred under reflux at 102 °C for 30 h. At the end of the reaction, 1.6 mL HCl was slowly added and cooled to room temperature. The products were then filtrated and washed three times with methanol. The washed water was collected and added to the filtered liquid. Methanol and *n*-C₄H₉OH were recovered via rotary evaporation from this mixed liquor. A certain amount of *n*-heptane was added to the obtained purplebrown viscous liquid, and then stirred under reflux at 90 °C for 2 h. It was then filtered while hot by pumping filtration. White sheet crystal was obtained after the filtrate was cooled to room temperature. The products were then dried by vacuum drying. 18.48 g of benzo-15-crown-5 was obtained with the yield of 37.1%.

Synthesis of 6-bromohexanoyl substituted benzo-15-crown-5: 6-Bromohexanoyl substituted benzo-15-crown-5 was synthesized according to the procedures described by Yang [32]. 362.26 g polyphosphoric acid was added into a 500 mL 3-mouth flask, and

stirred for 10 min at 60 °C in an oil bath. 11.83 g (0.044 mol) benzo-15-crown-5 and 8.58 g (0.044 mol) 6-bromohexanoic acid was successively added to the flask. A purplebrown solution was obtained after the reactant was maintained at 75 °C for 10 h. At the end of reaction, the flask was transferred to an ice bath. A certain amount of distilled water was subsequently added into the resulting solution drop by drop. Polyphosphoric acid was hydrolyzed under continuous stirring under this condition. The reaction product was then transferred to a 1000-mL of flask and extracted three times with chloroform. The chloroform layer was washed with saturated sodium carbonate and NaCl solution, respectively, and then dried with anhydrous sodium sulfate. Chloroform was recovered from the resulting solution via rotary evaporation. Finally, some diethyl ether was added to crystallize the product. 4.6 g of yellow crystal was obtained with the yield of 23.5%.

Synthesis of the crown ether functionalized II: [A(Benzo15C5)HIM][PF₆] was synthesized according to a method reported by Liu et al. [33]. A one to one mole ratio of 6-bromohexanoyl substituted benzo-15-crown-5 to 1-allylimidazole was added to a 10-mL of one-port flask with 5 mL acetone. The reactant was stirred under reflux at 50 °C for 36 h. The product was then reacted with potassium hexafluorophosphate in a one to one mole ratio for 24 h. Acetone was evaporated from the reaction system at the end of the reaction. The product was washed with 5 mL dichloromethane. The excess KBr was removed from the reaction system by centrifugal separation. The yield of [A(Benzo15C5)HIM][PF₆] was 63.2%.

2.4. Preparation of sol-gel coating

Prior to sol-gel coating, the protective polyimide layer was removed from the 6-cm-long fused-silica fiber by dipping it in acetone for 3 h. To expose the maximum number of silanol groups on the surface, the fiber was dipped in 1 M NaOH solution for 1 h, and then cleaned with water. Subsequently, it was placed in 0.1 M HCl

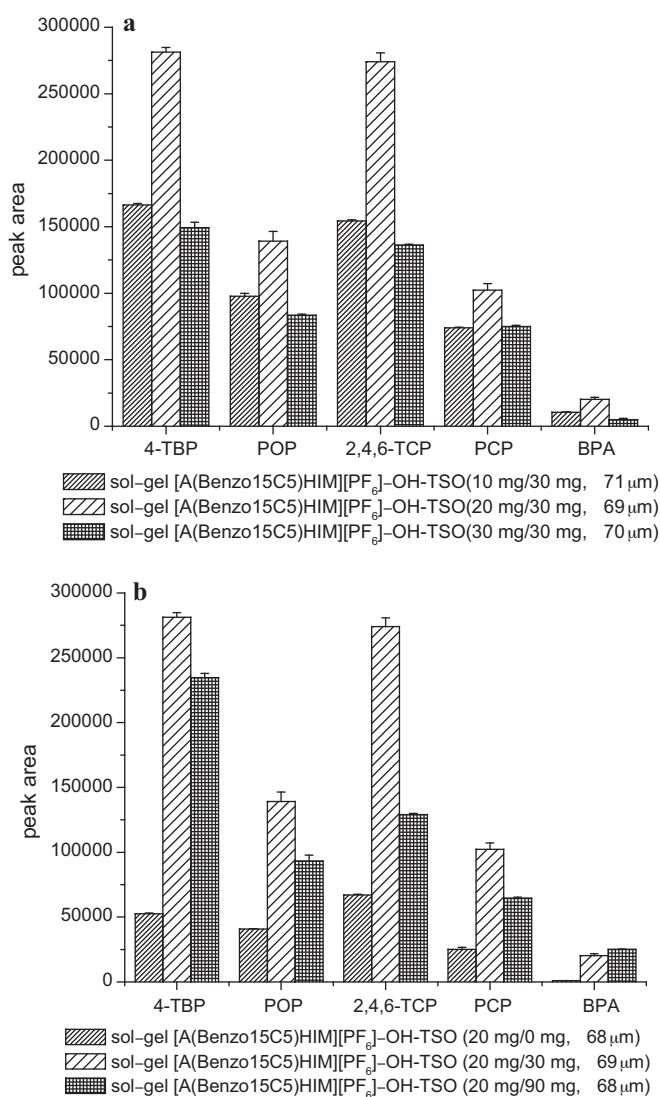


Fig. 2. (a) Comparison of the extraction efficiency of sol-gel-coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers containing different contents of [A(Benzo15C5)HIM][PF₆] for PEEs with the identical preparation procedure. (b) Comparison of the extraction efficiency of sol-gel-coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers containing different contents of OH-TSO for PEEs with the identical preparation procedure. SPME-GC conditions: injection temperature, 280 °C; FID temperature: 300 °C; oven temperature: 160 °C for 2 min, programmed at 10 °C min⁻¹ to 280 °C, held for another 8 min; split ratio, 1:20. Extraction time, 30 min; extraction temperature, 60 °C; desorption time, 5 min; pH 2; 40% (m/m) NaCl; magnetic stirring.

solution for 30 min to neutralize the excess NaOH, cleaned again, and dried at room temperature.

The sol-gel [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers were prepared as follows: 20 mg of [A(Benzo15C5)HIM][PF₆] was thoroughly dissolved in 800 μL methylene chloride; then 30 mg of OH-TSO, 100 μL of TEOS, 50 μL of KH-570, 10 μL of PMHS, 8 mg of benzophenone and 60 μL of TFA (containing 5% water, v/v) were added, respectively. The mixture was agitated by ultrasonic vibration for 5 min, and centrifuged at 12,000 rpm for another 5 min to remove the precipitate. The top clear sol solution was used for fiber coating. A sol-gel coating was formed on the outer surface of the treated fiber end, after the fiber was dipped vertically into the sol-gel solution for 3 h. For each fiber, this coating process was repeated several times until the desired thickness of the coating was obtained. After that the fibers were irradiated under ultraviolet light for 30 min, then placed in a desiccator for 12 h at room

temperature and conditioned in the GC injector at 280 °C under nitrogen protection for 2 h.

To investigate the impact of crown ether functionalized IL and OH-TSO on the coating performance, some other [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers were coated with a same procedure except that the mass ratio of IL to OH-TSO was 0 mg/30 mg, 10 mg/30 mg, 20 mg/30 mg, 30 mg/30 mg, 20 mg/0 mg and 20 mg/90 mg, respectively. The sol-gel-coated [AMIM][PF₆]-OH-TSO fibers for comparison were also prepared with an almost identical preparation procedure [25].

2.5. IR experiment

The sol-gel-derived OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers were conditioned at 280 °C under nitrogen protection for 2 h, and then dipped in water and methylene chloride for 2 h before the IR experiment, to remove the unbonded IL and other sol-gel components in the stationary phases. A section of the coating was harvested with a razor blade from the pretreated fiber, then ground and blended with potassium bromide (KBr). The KBr pellet spectra of these coatings were acquired with air as background at a resolution of 4 cm⁻¹ over the full mid-IR range (4000–400 cm⁻¹). In addition, the IR spectrum of pure [A(Benzo15C5)HIM][PF₆] was also recorded for comparison by liquid film method over the same frequency region and at the same resolution. The film of this IL was spread on a sodium chloride plate. The IR spectrum was acquired with the sodium chloride window as a background.

2.6. GC conditions

The analysis of fatty acids and alcohols was carried out on a Cp-sil 88-coated fused silica capillary column. The GC conditions for fatty acids were as follows: the injector temperature was 250 °C, the FID temperature was 300 °C, the oven temperature was maintained at 60 °C for 2 min, and then programmed to 200 °C at 5 °C min⁻¹, held for another 2 min. To analyze the alcohols, the injector and detector temperature were 250 °C and 300 °C, respectively. The oven temperature was maintained at 40 °C for 2 min, programmed to 140 °C at 5 °C min⁻¹, and then held there for 8 min. A capillary column coated with SE-54 was used for the separation of PEEs, phthalate esters (PAEs) and aromatic amines. When PEEs were analyzed, the injection port temperature was maintained at 250 °C and the detector temperature was at 300 °C. The oven temperature was held at 180 °C for 2 min, increased to 280 °C at 10 °C min⁻¹, and then held for another 8 min. The separation conditions for PAEs were as follows: both the injector and detector temperature were maintained at 300 °C, the oven temperature was maintained at 150 °C for 2 min, then programmed at 15 °C min⁻¹ to 300 °C, and held for another 20 min. To analyze the aromatic amines, the injector, oven and detector temperatures were maintained at 250 °C, 140 °C and 260 °C, respectively. The carrier gas was nitrogen at a linear velocity of 12–15 cm s⁻¹ in the 1:20 split mode for all the analyses.

2.7. Preparation of standard solutions

Individual stock solutions containing 10 mg mL⁻¹ each of 1-propanol, isobutyl alcohol, 1-butyl alcohol, isoamyl alcohol, 1-amyl alcohol, 1-hexanol and 1 mg mL⁻¹ of 1-octanol were prepared in methanol. Individual stock solutions containing 10 mg mL⁻¹ each of isobutyric acid, valeric acid, hexanoic acid and 1 mg mL⁻¹ each of heptanoic acid, octanoic acid were also prepared in methanol. Stock solutions of PEEs and PAEs were prepared by dissolving 10 mg of each compound in 10 mL of methanol to reach a concentration of 1 mg mL⁻¹. Aromatic amines were dissolved in acetonitrile. The final concentration of this stock solution was 1 mg mL⁻¹.

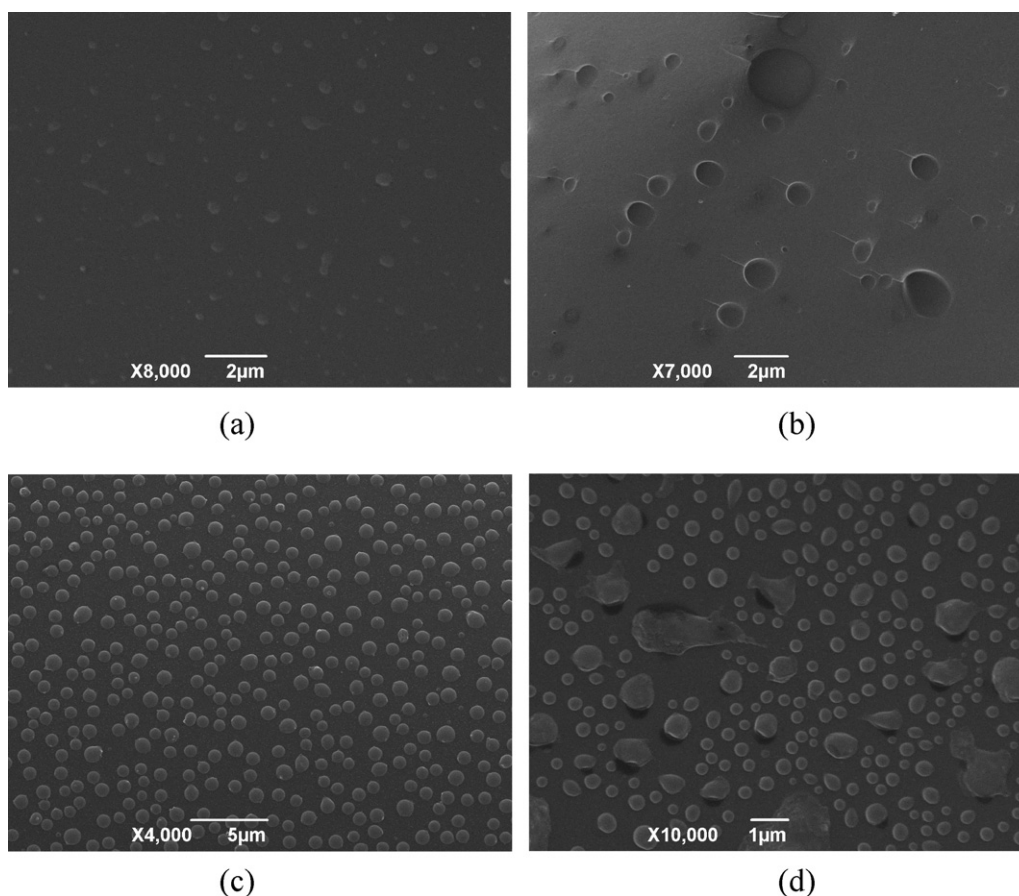


Fig. 3. SEM images of the sol-gel-derived OH-TSO (a), [A(Benzo15C5)HIM][PF₆] (b) and [A(Benzo15C5)HIM][PF₆]-OH-TSO (c: 4000×; d: 10000×) fibers.

2.8. SPME procedures

For PEEs and PAEs analysis, an 8- μ L portion of standard solution was diluted with 8 mL deionized water in a 10 mL amber vial containing 3 g NaCl to reach a concentration of 1 μ g mL⁻¹. For the analysis of fatty acids and alcohols, 10 μ L standard solutions were added to 5 mL deionized water containing 2 g NaCl to produce a water sample of 2 μ g mL⁻¹. For the analysis of aromatic amines, the standard solution, deionized water and NaCl were 5 μ L, 5 mL and 2 g, respectively. The concentration of this water sample was 1 μ g mL⁻¹. The pH of phenols and fatty acids was adjusted to 2 with HCl, and that of aromatic amines was adjusted to 13 with NaOH. To prevent the samples from being adsorbed on the glass wall, the amber vials were acid washed and silanized prior to the SPME experiments. The extraction of PEEs and PAEs was carried

Table 1
Fiber-to-fiber and run-to-run reproducibility of the sol-gel-derived chemically bonded [A(benzo15C5)HIM][PF₆]-OH-TSO fibers.

Compounds	Reproducibility (RSD, %)	
	Fiber-to-fiber ($n = 3^a$, 50 μ m)	Run-to-run ($n = 5^b$, 62 μ m)
1-Propanol	2.5	3.5
Isobutyl alcohol	6.8	4.8
1-Butyl alcohol	7.5	5.7
Isoamyl alcohol	4.9	5.2
1-Amyl alcohol	2.1	5.3
1-Hexanol	5.0	7.6
1-Octanol	2.9	7.9

SPME-GC conditions are the same as in Fig. 4.

^a $n = 3$ represents three fibers obtained from the same batch.

^b $n = 5$ represents five duplicate extractions with the same fiber.

out by direct immersion of the fibers in the aqueous sample, and the extraction of fatty acids, alcohols and aromatic amines was performed by exposure of the fiber to the headspace of the water solution.

3. Results and discussion

3.1. Reactive mechanism of sol-gel coatings

In sol-gel approach, the stationary phase coating is chemically bonded to the surface of the fiber under extremely mild thermal conditions [34,35]. Two major sets of reaction take place during the sol-gel process: (1) hydrolysis of the precursor and (2) polycondensation of the hydrolyzed products and other sol-gel active ingredients. Unlike the commonly used sol-gel method, in which only one metal alkoxide is used as the precursor to produce organic-inorganic hybrid coating, our process involves two different silica monomers (TEOS and KH-570) as co-precursors. TEOS considered as a most widely used metal precursor in sol-gel reaction can be readily hydrolyzed and polycondensed to form three-dimensional network under relatively mild conditions. KH-570, which contains both vinyl and trimethoxysilyl substituents on the tag end can be served as coupling agent during the sol-gel reaction process. In this work, the crown ether functionalized IL can be chemically bonded to other coating ingredients through the free radical cross-linking reaction between KH-570 and [A(Benzo15C5)HIM][PF₆]. A simplified scheme of the sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO polymeric coatings was schematically represented in supplementary Fig. S1.

The IR absorption bands of [A(Benzo15C5)HIM][PF₆] characteristic for aromatic C=C stretch (1596 cm⁻¹, 1515 cm⁻¹ and

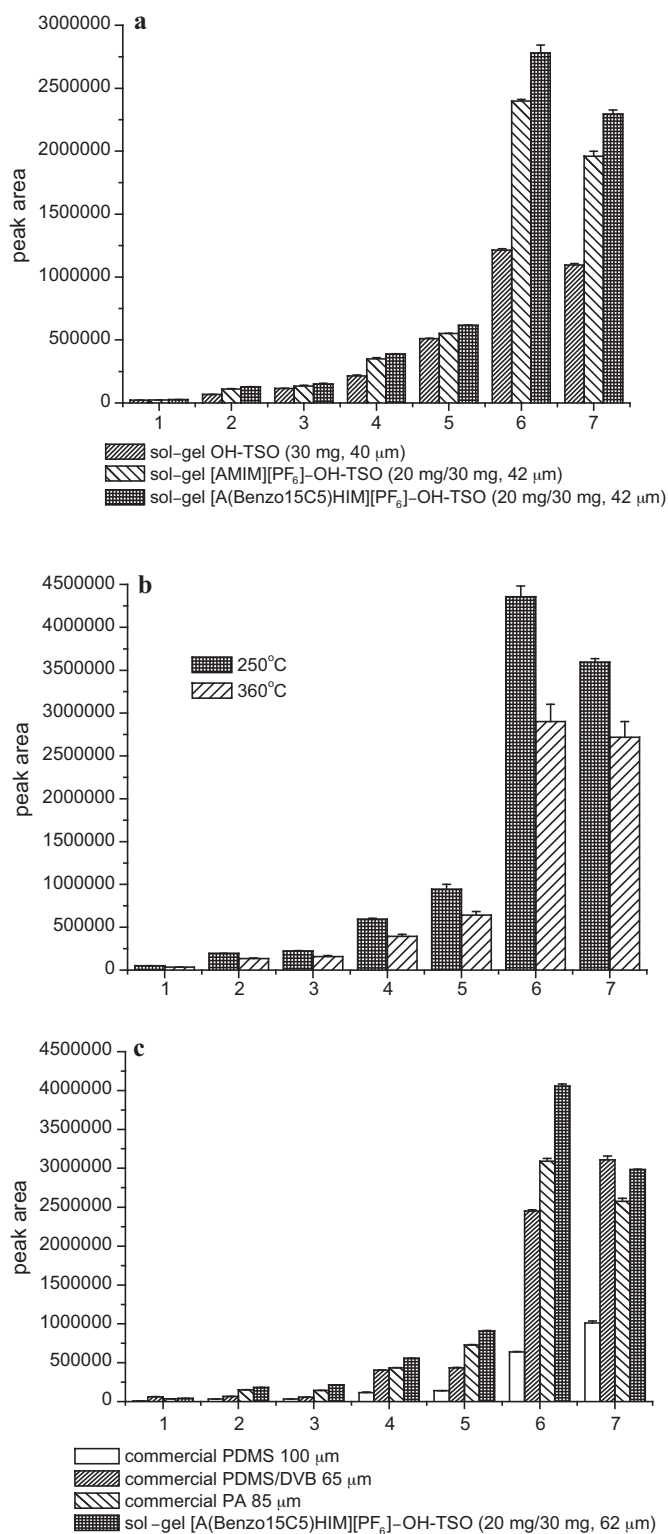


Fig. 4. (a) Comparison of the extraction capability of the sol-gel coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure for the extraction of alcohols in water. (b) Comparison of the amounts of alcohols extracted by the sol-gel coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber after being conditioned at 250 °C and 360 °C, respectively. (c) Comparison of the extraction efficiencies of the sol-gel derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber with commercial PDMS, PDMS/DVB and PA fibers for alcohols. SPME-GC conditions: injection temperature, 250 °C; FID temperature: 300 °C; oven temperature: 40 °C for 2 min, programmed at 5 °C min⁻¹ to 140 °C, held for another 8 min; split ratio, 1:20. Extraction time, 30 min; extraction temperature, 30 °C; desorption time, 5 min; pH 7; 40% (m/m) NaCl; magnetic stirring. (1) 1-propanol; (2) isobutyl alcohol; (3) 1-butyl alcohol; (4) isoamyl alcohol; (5) 1-amyl alcohol; (6) 1-hexanol; (7) 1-octanol.

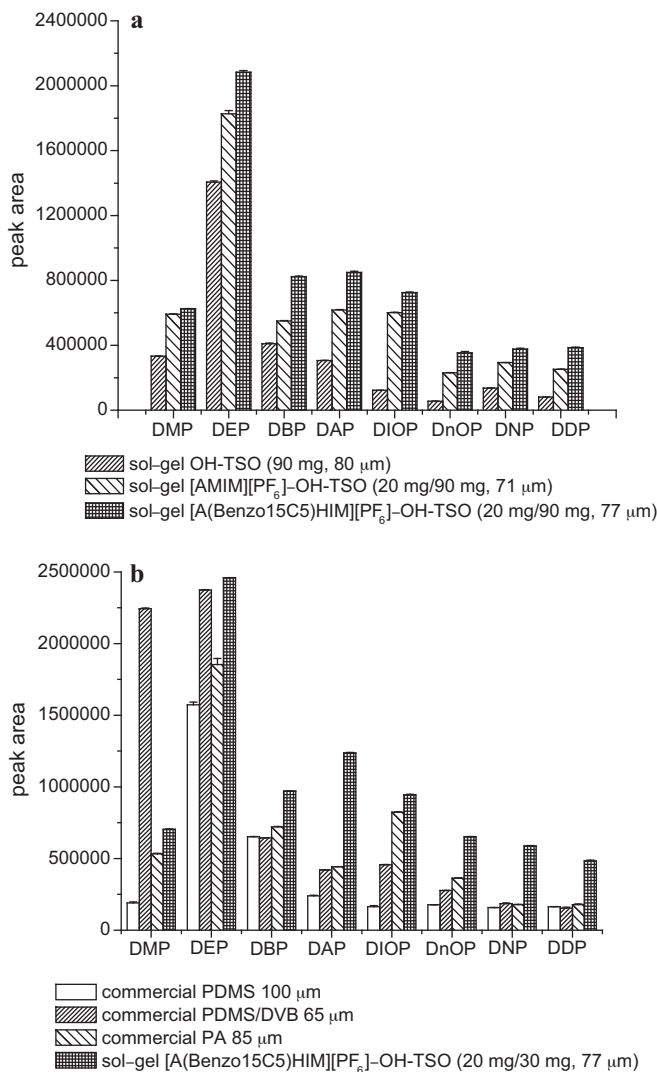


Fig. 5. (a) Comparison of the amounts of PAEs extracted by the sol-gel coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. (b) Comparison of the extraction efficiencies of sol-gel derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber with commercial PDMS, PDMS/DVB and PA fibers for PAEs. SPME-GC conditions: injection temperature, 300 °C; oven temperature: 150 °C for 2 min, programmed at 15 °C min⁻¹ to 300 °C, held for another 20 min; split ratio, 1:20. Extraction time, 40 min; extraction temperature, 30 °C; desorption time, 5 min; pH 7; 40% (m/m) NaCl; magnetic stirring.

1457 cm⁻¹, imidazolium C=N stretch (1561 cm⁻¹ and 1430 cm⁻¹), benzo-15-crown-5 Ar-O-C and C-O-C symmetric (1268 cm⁻¹) and anti-symmetric (1130 cm⁻¹) stretching vibrations, and PF₆⁻ (841 cm⁻¹, 557 cm⁻¹) were also appeared in sol-gel derived [A(Benzo15C5)HIM][PF₆]-OH-TSO coatings (supplementary Fig. S2), confirming the successful chemical binding of crown ether functionalized IL with other sol-gel active ingredients.

3.2. Optimization of coating preparation

In SPME, the selectivity and extraction efficiency of the sol-gel coating were mainly influenced by the structure characteristics and relative content of functional molecule used as stationary phase material. In our study, a uniform and stable [A(Benzo15C5)HIM][PF₆]-OH-TSO coated fiber can be achieved through optimization of the content of [A(Benzo15C5)HIM][PF₆]

and OH-TSO. Fig. 2a shows the amounts of PEEs extracted by sol-gel crown ether functionalized IL-based SPME fibers containing different masses of [A(Benzo15C5)HIM][PF₆]. It was shown that the extraction capability of these novel coatings were highest when the content of [A(Benzo15C5)HIM][PF₆] added to the sol solution was 20 mg. The response obtained by 30 mg/30 mg [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber was obviously lower than that achieved by 20 mg/30 mg [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber. This may be attributed to the fact that too much IL and too little OH-TSO in the sol solution will lead to a decrease in the spreadability, and thus an increase in the extent of cracking of the sol-gel derived [A(Benzo15C5)HIM][PF₆]-OH-TSO coating during the gelation and aging stages. Fig. 2b compares the extraction efficiency of sol-gel crown ether functionalized IL-based SPME fibers containing different masses of OH-TSO. As shown in the figure, the extraction capability of these coatings was highest when the content of OH-TSO added to the sol solution was 30 mg. When the content of OH-TSO increased to 90 mg, the extraction efficiency declined evidently because the polarity of the sol-gel derived [A(Benzo15C5)HIM][PF₆]-OH-TSO coating declined with the increase of OH-TSO. These results obtained from Fig. 2 demonstrated that a suitable mass ratio of [A(Benzo15C5)HIM][PF₆] to OH-TSO in coating is very important for the improvement of the selectivity and sensitivity of the IL-based sol-gel fibers. Therefore, 20 mg/30 mg [A(Benzo15C5)HIM][PF₆]-OH-TSO coated fiber was chosen for subsequent SPME-GC experiments.

3.3. Characteristics of IL-based sol-gel coating

3.3.1. Surface morphology

Fig. 3 shows the surface morphology of sol-gel derived OH-TSO (30 mg), [A(Benzo15C5)HIM][PF₆] (20 mg) and [A(Benzo15C5)HIM][PF₆]-OH-TSO (20 mg/30 mg) fibers prepared with the same procedures. To remove the unbonded sol-gel ingredients, both fibers were conditioned at 280 °C under nitrogen atmosphere for 2 h before acquiring the SEM images. As shown in Fig. 3, the surface morphology of the sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO coating is much different from that of OH-TSO and [A(Benzo15C5)HIM][PF₆] coatings. It has smooth surface with a large number of pores distributed below the “bubble-like” coating surface (Fig. 3c). The pores appear evidently when the bubbles were broken and the debris was removed from the surface (Fig. 3d). It is also very different from that of the sol-gel derived [AMIM][PF₆]-OH-TSO fibers prepared in our previous work [25], indicating that the steric hindrance of cation has great influence on the surface morphology of the produced sol-gel IL-based coatings. [A(Benzo15C5)HIM]⁺ has much larger molecular weight than [AMIM]⁺, and the steric hindrance for the formation of π - π stacks of imidazolium rings is larger for the former than the latter, leading to a different mode of self-assembly of ILs in the sol-gel coatings.

3.3.2. Thermal stability

The thermal behavior of the sol-gel [A(Benzo15C5)HIM][PF₆]-OH-TSO coatings was measured by thermogravimetric analysis at a rate of 10 °C min⁻¹ in nitrogen atmosphere (supplementary Fig. S3). Three thermal events are visible: The first mass loss occurred at 195 °C, could be attributed to the release of low molecular mass reaction products absorbed or entrapped inside the pore structure of the polymer. The second weight loss happened at 345 °C caused by the removal of [A(Benzo15C5)HIM][PF₆] chemically bonded to the organic-inorganic hybrid coating. The third occurred at 425 °C owing to the decomposition of OH-TSO. Compared with the sol-gel coated [AMIM][PF₆]-OH-TSO coating (320 °C) prepared in our previous work [25], the [A(Benzo15C5)HIM][PF₆]-OH-TSO

composite is more stable at higher temperatures (345 °C). This may be attributed to the special molecular structure of the 6'-oxo-benzo-15-crown-5 hexyl functional groups in the imidazole cation.

3.3.3. Chemical stability

The chemical stability of the sol-gel [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers was evaluated by comparing its extraction ability before and after dipping in distilled water, 1 M HCl, 1 M NaOH and CH₂Cl₂ for 2 h, respectively. The result indicates that it has good chemical stability to resist water, acid, alkali and solvent washing (supplementary Fig. S4). This is attributed not only to the three-dimensional network structure of the sol-gel coatings, the strong chemical binding between the coating and the fused-silica fiber, but also to the unique physical and chemical characteristics of the crown ether functionalized IL itself.

3.3.4. Coating preparation reproducibility

Table 1 represents the fiber-to-fiber and run-to-run reproducibility of the sol-gel-coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers. The reproducibility was estimated by the relative standard deviation (RSD) values. To examine the fiber-to-fiber reproducibility, three sol-gel [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers (50 μ m) prepared in the same batch were selected for the extraction of alcohols from aqueous solution. The run-to-run repeatability was calculated based on five duplicate extractions and analyses of alcohols from water samples using a 62 μ m of [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber. These results show that the reproducibility of the prepared SPME fibers (RSD <8%) is satisfactory, not only for the same fibers but also for different fibers.

3.3.5. Selectivity of [A(Benzo15C5)HIM][PF₆]-OH-TSO coating

3.3.5.1. SPME-GC analysis of alcohols. Fig. 4a compares the amounts of alcohols extracted by the sol-gel-coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. As revealed from the figure, the sol-gel OH-TSO fiber has a much lower response to alcohols than does the sol-gel [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers. The result shows that IL introduced to the sol-gel coating plays a very important role in the extraction. The [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber provides higher response to alcohols than does the [AMIM][PF₆]-OH-TSO fiber, which should be attributed to the strong hydrogen bonding interaction between the investigated alcohols and the oxygen heteroatoms on the crown ether ring.

To further confirm the contribution of crown ether functionalized IL to the extraction, we compared the amounts of alcohols extracted by sol-gel coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber after being conditioned at 250 °C and 360 °C (above the decomposition temperature of this IL) for 2 h, respectively (Fig. 4b). As shown in this figure, the extraction efficiency of the [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber had an evident decline after being conditioned at 360 °C for 2 h. This can be explained by the fact that crown ether functionalized IL did not participate in the extraction process since they had been removed from the coating at this high temperature.

Fig. 4c compares the extraction efficiencies of the sol-gel derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber with commercial PDMS, PDMS/DVB and PA fibers for the analysis of alcohols. As revealed from the figure, the [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber provided much higher response to alcohols than did the three tested commercial fibers. This may be results from the strong electrostatic and hydrogen bonding interactions provided by [A(Benzo15C5)HIM][PF₆] as well as the enhanced surface area

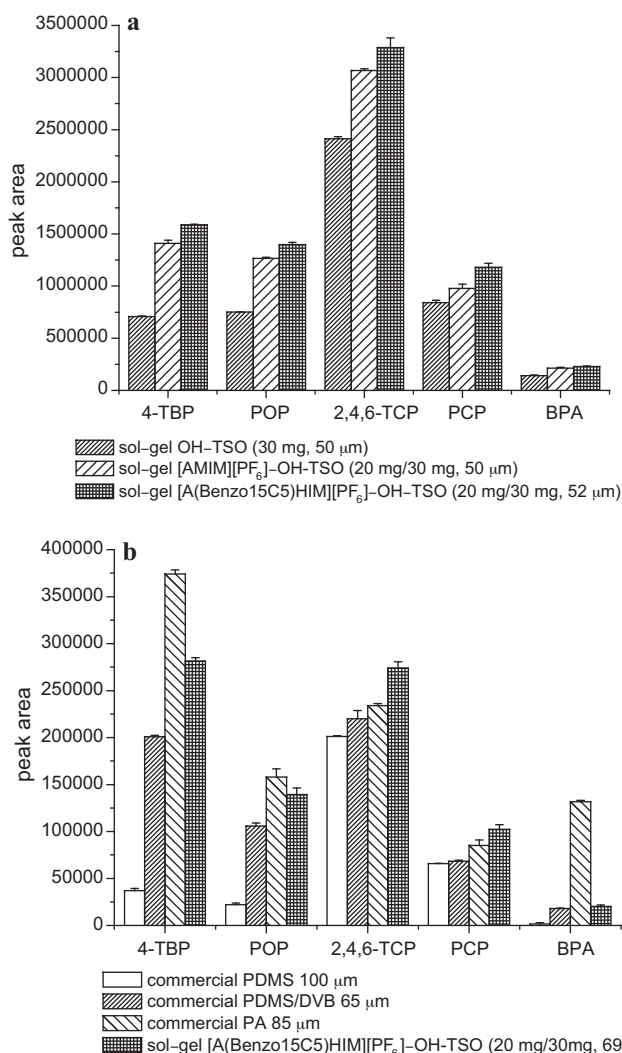


Fig. 6. (a) Comparison of the amounts of PEEs extracted by the sol-gel-coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. (b) Comparison of the extraction efficiencies of sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber with commercial PDMS, PDMS/DVB and PA fibers for PEEs. SPME conditions are the same as in Fig. 2.

and sample capacity of sol-gel coating in comparison with other materials prepared by traditional coating methods.

3.3.5.2. SPME-GC analysis of PAEs. Fig. 5a compares the amounts of PAEs extracted by the sol-gel-coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. As revealed from the figure, the response provided by the [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber is highest. The conjugated π electric system and the electronegative effect of oxygen heteroatoms on benzo-15-crown-5 resulted in good selectivity for PAEs with aromatic ring and medium polar character. Similar experiments reveal that the [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber also has higher extraction efficiency to most of the PAEs than does the commercial PDMS, PDMS/DVB and PA fibers (Fig. 5b).

3.3.5.3. SPME-GC analysis of PEEs. Fig. 6a compares the amounts of PEEs extracted by the sol-gel-coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. As revealed from the figure, the [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber provided much higher response to PEEs than did the sol-gel OH-TSO and [AMIM][PF₆]-OH-TSO fibers. Its better selectivity and sensitivity

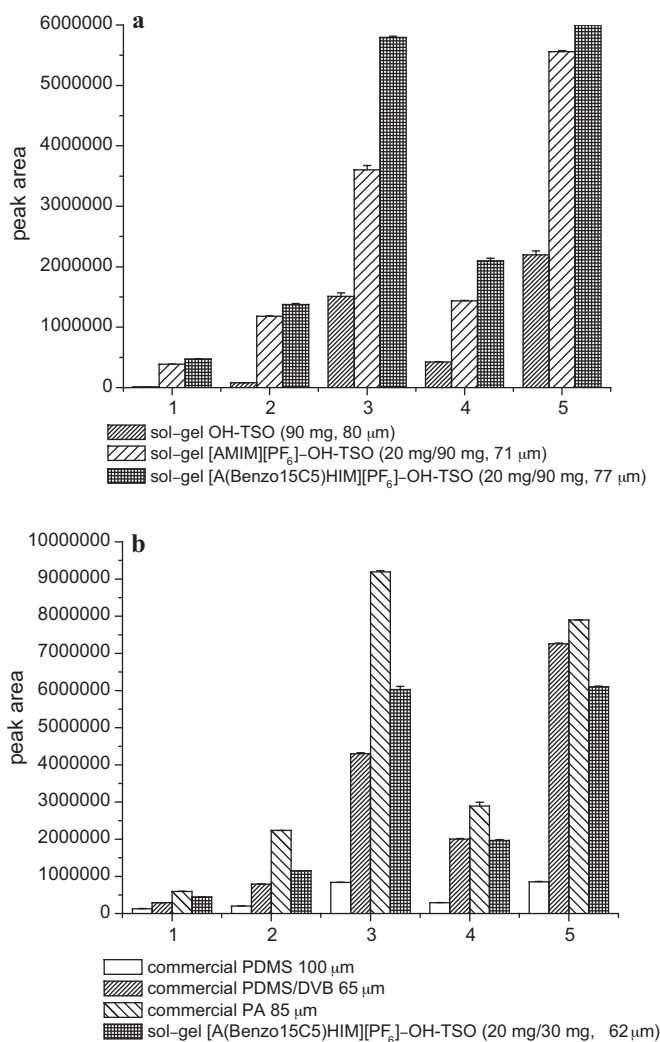


Fig. 7. (a) Comparison of the amounts of fatty acids extracted by the sol-gel-coated OH-TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. (b) Comparison of the extraction efficiencies of sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber with commercial PDMS, PDMS/DVB and PA fibers for fatty acids. SPME-GC conditions: injection temperature, 250 °C; FID temperature: 300 °C; oven temperature: 60 °C for 2 min, programmed at 5 °C min⁻¹ to 200 °C, held for another 2 min; split ratio, 1:20. Extraction time, 30 min; extraction temperature, 60 °C; desorption time, 5 min; pH 2; 40% (m/m) NaCl; magnetic stirring. (1) Isobutyric acid; (2) valeric acid; (3) hexanoic acid; (4) heptanoic acid; (5) octanoic acid.

to these polar compounds investigated should be attributed to the strong electrostatic interaction, hydrogen bonding interaction and π - π interaction derived from not only the unique anion and cation properties of IL but also the special structure characteristics of benzo-15-crown-5 functional groups.

Fig. 6b compares the extraction efficiencies of the sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber with commercial PDMS, PDMS/DVB and PA fibers for PEEs. As revealed from the figure, the extraction ability of this sol-gel coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber was much higher than that of commercially available PDMS and PDMS-DVB fibers. It was also higher for less polar 2,4,6-TCP and PCP in comparison with PA fiber. However, it was somewhat lower for more polar 4-TBP, POP and BPA than PA fiber due to its weaker polarity and thinner film thickness.

3.3.5.4. SPME-GC analysis of fatty acids. Fig. 7a compares the amounts of fatty acids extracted by the sol-gel-coated OH-

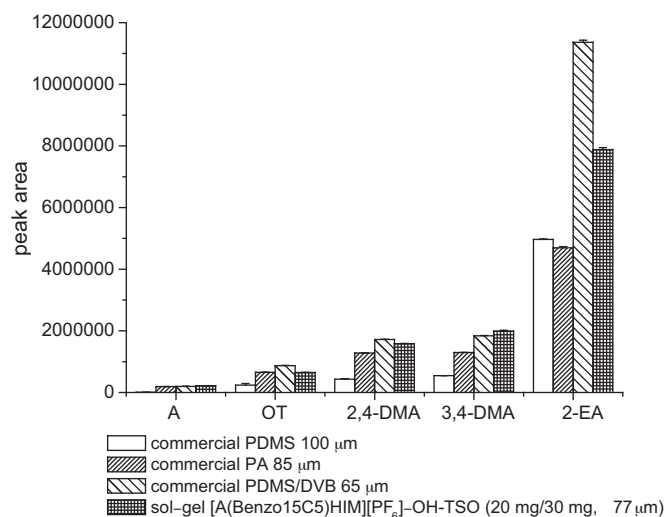


Fig. 8. Comparison of the extraction efficiencies of sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with commercial PDMS, PDMS-DVB and PA fibers for the analysis of aromatic amine under the same conditions. SPME-GC conditions: injection temperature, 250 °C; FID temperature: 260 °C; oven temperature: 140 °C; split ratio, 1:20. Extraction time, 20 min; extraction temperature, 40 °C; desorption time, 5 min; pH 11; 40% (m/m) NaCl; magnetic stirring.

TSO, [AMIM][PF₆]-OH-TSO and [A(Benzo15C5)HIM][PF₆]-OH-TSO fibers with the identical preparation procedure. As shown in this figure, the [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber provided much higher response to fatty acids than did the OH-TSO and [AMIM][PF₆]-OH-TSO fibers. Similar experiments showed that it also exhibited superior extraction efficiency to fatty acids than did the commercial PDMS and PDMS/DVB fibers (Fig. 7b). Although the polarity of the sol-gel-derived [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber is greatly enhanced due to the introduction of benzo-15-crown-5 functional group in the IL structure, it is still lower than commercial PA fiber (Fig. 7b). Therefore, the selectivity and extraction efficiency of this crown ether functionalized IL-based fiber for fatty acids was a little lower than commercial PA fiber.

3.3.5.5. SPME-GC analysis of aromatic amines. Fig. 8 compares the extraction efficiencies of sol-gel-coated [A(Benzo15C5)HIM][PF₆]-OH-TSO with commercial PDMS, PDMS/DVB and PA fibers for the analysis of aromatic amines. As revealed from the figure, the extraction ability of this sol-gel-derived crown ether functionalized IL-based organic-inorganic hybrid coating was superior to that of PDMS and PA fibers. It was almost identical to that of PDMS/DVB fiber except the less polar 2-EA.

The results obtained in this part indicated that the developed sol-gel coated [A(Benzo15C5)HIM][PF₆]-OH-TSO fiber showed excellent selectivity and extraction efficiency for polar to medium polar compounds, such as alcohols, PAEs, PEEs, fatty acids and aromatic amines. The high selectivity of this novel coating can be explained as follows: Firstly, the unique anion and cation properties of ILs can provide electrostatic interactions for the compounds easy to ionization, such as PEEs, fatty acid and aromatic amines. Secondly, the strong electronegative effect of heteroatoms on the crown ether ring can offer hydrogen bonding interaction with alcohol, PEEs, fatty acid and aromatic amines. Thirdly, the conjugated π electric system of benzo-15-crown-5 can provide π - π interaction with compounds containing aromatic rings, such as PAEs, PEEs and aromatic amines. Lastly, the three-dimensional network structure of sol-gel coating can provide larger surface area, and thus higher adsorption capacity for this fiber.

4. Conclusions

This is the first report on the creation and use of sol-gel crown ether functionalized IL-based organic-inorganic hybrid coatings in solid-phase microextraction. Due to the unique properties of both IL and benzo-15-crown-5 functional group, this novel coating exhibited high selectivity and extraction capacity for polar to medium polar compounds, such as alcohols, PAEs, PEEs, fatty acids and aromatic amines. It also had porous surface structure, high thermal stability (to 340 °C), wide pH use range, good solvent resistance and satisfactory coating preparation reproducibility.

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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.2011.03.048](https://doi.org/10.1016/j.chroma.2011.03.048).

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