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Poly(ionic liquid) embedded particles as efficient solid phase microextraction phases of polar and aromatic analytes

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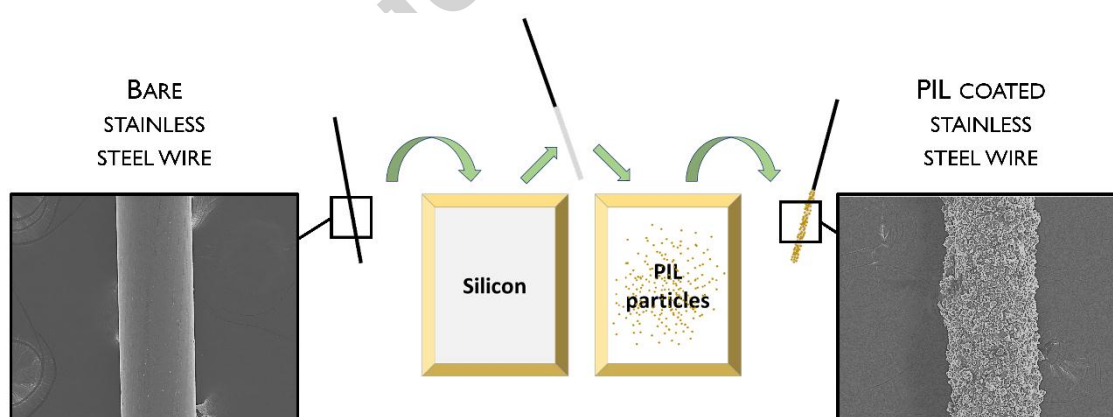
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Abstract

In this work, a facile preparation of SPME fibers with increased surface area is presented. The SPME fibers were prepared by grinding poly(ionic liquids) (PILs) to obtain particles of 1 to 16 μm and, with the aid of a silicon adhesive, attach these particles to a steel wire support. Three different PILs, poly(1-vinyl-3-benzylimidazolium-co-styrene bromide) [(poly(ViBnIm-co-Sty Br)], poly(1-vinyl-3-benzylimidazolium-co-styrene bis(trifluoromethanesulfonyl)imide) [poly(ViBnIm-co-Sty TFSI)] and poly(diallyldimethylamine bis(trifluoromethanesulfonyl)imide)

[poly(Pyrr₁₁ TFSI)], were used. The first two PILs were obtained by reversible addition–fragmentation chain transfer polymerization followed by metathesis reactions. The thicknesses of the prepared fibers were found to be $19 \pm 4 \mu\text{m}$ and 85 % of the particles used have diameters between 2-10 μm . The prepared fibers were tested by performing the headspace extraction of two standard solutions, one containing a mixture of alcohols with different chain lengths, and the other a mixture of aromatic compounds, leading to sorption times of 10 – 15 min due the large surface area attained with this method. PILs with aromatic moieties containing the bromide anion showed high selectivity towards polar compounds, due to the hydrogen basicity of the anion, and also towards aromatic analytes, due to the aromatic nature of styrene moieties and the cation pendant groups. The limits of detection fall in the sub ppb level, while relative standard deviations and reproducibility from fiber-to-fiber found maximums of 16.2 % and 22.5 %, respectively. Furthermore, the PIL based fibers showed up to 90 % higher extraction efficiencies compared to the commercial fibers of polydimethylsiloxane and polyacrylate.

Graphical abstract



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Keywords: Solid phase microextraction, Poly(ionic liquids), Increased Surface Area, BTEX, Alcohols, Gas chromatography

1. Introduction

The development of new sorbent phases for the detection of target compounds in complex mixtures is one of the main challenges in modern analytical chemistry [1]. Among the existing pre-concentration techniques, solid phase microextraction (SPME) stands out for its simplicity, efficiency and robustness, and since its introduction in the early 90's [2], it has gathered increasing interest in different fields such as metabolomics [3], environmental [4], food analysis [5] or health [6] sciences. Amongst the several SPME configurations [7], the fiber configuration is undoubtedly the most widely used, not only due to its simple use in gas, liquid or semi-solid samples, but also to the easiness of introduction of the extracted fraction in the GC [8]. Nowadays, polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA) or polyethyleneglycol (PEG) are among the most used polymeric coatings [9], nonetheless, the increasingly demanding of analytical sensitivity requires new fiber coatings with improved performances, such as selectivity and increased concentration capacity, combined with high mechanical and thermal stability [10].

Currently, several fiber coating fabrication methods are being used to process a plethora of materials [11,12], with ionic liquids (ILs) and poly(ionic liquids) (PILs) [13] being amongst the most studied ones, mainly due to their high thermal stability and easy chemical tunability. ILs were first tested as SPME coatings for the analysis of a mixture of aromatic compounds present in paints [14], however, the high desorption step temperatures (200-300 °C) prevents their reuse. As a result, the polymeric forms of ILs, introduced in SPME by Anderson and co-workers [15], demonstrated superior mechanical and thermal stability, and since then they have been successfully applied as SPME fibers [16–18] to extract and analyze a wide range of analytes [19–21]. Nonetheless, despite the well know affinity of ILs/PILs for polar compounds [22,23],

only a few works address the extraction of polar compounds using PILs. Furthermore, methods addressing the increase in coating surface area or heterogeneity are still scarce. Wanigasekara et al. [24], for example, used [1-vinyl-3-benzylimidazolium] with other polar IL monomers chemically bonded to 5 μm silica particles with 10 nm pore size and surface area of 310 $\text{m}^2 \text{g}^{-1}$. These large surface area fibers were used to analyze short-chain alcohols down to the 10 ppb level. Regarding the selectivity towards polar compounds, Meng et al. [25] explored the role of the counter anion and the effect of mixing PILs with different anions. Although the authors were able to increase selectivity towards polar analytes while using halogen anions, a noticeable decrease in the thermal stability of these fibers was observed, and desorption temperatures higher than 175 $^{\circ}\text{C}$ could not be used. Overcoming thermal stability, Feng et al. [26] prepared a fiber composed of a crosslinked PIL for the headspace extraction of polar compounds from aqueous matrices and beverages. The crosslinked material along with the halogen nature of the anions showed improved sensitivity, reproducibility and thermal stability.

Taking this into account, in this work we present an easy, cost-effective polar selective PIL based SPME coating fabrication methodology. The SPME fibers were prepared by grinding two different PILs, one based on the imidazolium and the other based on pyrrolidinium cation, and with the aid of a silicon adhesive these particles were attached to a steel wire support. This technique allows the creation of fibers with increased surface area, resulting in quick and excellent extraction efficiencies. Despite our recent publication on pyrrolidinium-based SPME fibers [18], this is the first time that poly(Pyrr₁₁ TFSI) obtained from the commercial chloride based polymer is used as SPME extraction phase. The prepared PIL based SPME fibers were tested against two sets of aqueous solutions containing aromatic compounds (benzene, ethylbenzene, xylene and toluene (BTEX)) and a range of alcohols (ethanol, butanol, heptanol, octanol

and benzyl alcohol) (Table S1). These analytes chemical structures were chosen due to the possible interactions with the PIL coating, so that hydrogen bond capacity, hydrophobic/hydrophilic interactions, π - π interaction, cation and anion influence could be evaluated. Furthermore, the fabricated fibers were compared with commercial fibers composed of polydimethylsiloxane and polyacrylate, two available but distinct SPME phases.

2. Experimental

2.1 Materials:

Source and grade of the used chemicals and reagents were as follows: 1-vinylimidazole (> 99 %), benzyl bromide (> 98 %), styrene (> 99 %), ethyl-2-bromopropionate (99 %), potassium ethyl xanthogenate (96 %), poly(diallyldimethylammonium chloride) [poly(Pyrr₁₁ Cl)] solution (average Mw 400,000–500,000, 20 wt.% in H₂O), acetone (99.5 %), dry dimethylformamide (99.8 %), diethyl ether (99.8 %), dichloromethane (99.9 %), ethyl acetate (99.8 %), methanol (99.8 %), 1-butanol (99.9 %), 2-heptanol (98 %), 1-octanol (99.7 %) and benzyl alcohol (99.8 %) were purchased from Sigma-Aldrich. Acetonitrile (99.8 %) and ethanol were supplied by Carlo Erba Reagents. Lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) (99 %) was purchased from IOLITEC. Benzene (B) (99 %) was provided by Riedel-de Haen. Neutral silicon adhesive was purchased from Axton. Ethylbenzene (E) (99 %), toluene (T) (99 %) and p-xylene (X) (99 %) were obtained from Merck. Chloroform-d (CDCl₃) (\geq 99.8) and dimethyl sulfoxide *d*₆ (DMSO-*d*₆) (99.8 %) were supplied by Cambridge Isotope Laboratories, Inc. The commercial fibers PDMS (7 μ m) (PDMS7) and PA (85 μ m) (PA85) and the Supelco SPME fiber holder were purchased from Supelco (Aldrich, Bellefonte, PA,

USA). All reagents were used as received. Double distilled water, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment, was used in all experiments.

2.2 Synthesis and characterization of poly(ionic liquids)

2.2.1 Synthesis of poly(ViBnIm-co-Sty TFSI)

Poly(ViBnIm-co-Sty TFSI) was obtained as reported elsewhere [17] and it is detailed in the supporting information. Briefly, for the synthesis of [1-vinyl-3-benzylimidazolium bromide] ([ViBnIm]Br), 1-vinylimidazole was reacted in equimolar quantities with benzyl bromide in ethanol during 3 h at 60 °C. Afterwards, poly(ViBnIm-co-Sty Br) was obtained in dimethylformamide by RAFT copolymerization of [ViBnIm]Br with styrene (Sty), using a xanthate based chain transfer agent (CTA) [27,28], during 48 h at 70 °C. The obtained poly(ViBnIm-co-Sty Br) was reacted with LiTFSI to obtain poly(ViBnIm-co-Sty TFSI) that was dried at $T = 40\text{ °C}$ and $p = 1\text{ Pa}$ until constant weight was attained (Figure 1a).

2.2.2 Preparation of poly(Pyrr₁₁ TFSI)

The preparation of poly(Pyrr₁₁ TFSI) was performed based on a previously reported metathesis reaction [29]. Briefly, a 1.2 molar excess of LiTFSI salt was dissolved in water and added dropwise to a 1 molar amount of the commercial poly(Pyrr₁₁ Cl) (Figure 1b). After vigorous stirring, the precipitate was washed several times with water and dried at $T = 40\text{ °C}$ and $p = 1\text{ Pa}$ until constant weight was attained.

2.3 SPME fiber coating preparation

To prepare a mechanically stable fiber, steel wire was cut into 9 cm pieces and cleaned with deionized water, acetone, dichloromethane and methanol, and kept in an

oven at 60 °C during 2h to evaporate all residual solvents. The solid PILs were ground using an electric coffee grinder and an adhesive (neutral silicon with a polydimethylsiloxane base) was used to hold the particles into the metal wire. Briefly, 1 cm of wire was vertically inserted into a toluene diluted silicon solution (50 % w/v) and slowly removed so that a uniform coating was achieved. Then, the thin coated wire was rolled on top of PIL particles so that a layer of particles adheres on top of the silicon. The prepared fiber was placed in an oven at 60 °C during 8h to evaporate the solvent and then transferred to the gas chromatograph injection port, which was kept at 220 °C during 1h to complete the conditioning of the fiber. For comparison purposes, a fiber with a homogeneous film coating of VBSTFSI-F was also prepared using a spray-coating technique [17]. All the fibers were analyzed using a Hitachi S2400 scanning electron microscopy (SEM) with Bruker light elements EDS detector.

2.4 Headspace – SPME methodology

Standard stock solutions of aqueous alcohols and BTEX were separately prepared and stored. For the SPME procedure, 5 mL of each standard solution were transferred into 10 mL glass vials and the HS-SPME was performed by exposing the fiber to the headspace of the sample. After extraction, the fibers were immediately inserted into the GC injector and kept there for 3 min. Between each set of experiments, a blank injection was used to confirm the absence of analytes from previous extractions. All the experiments were done in triplicate to estimate uncertainties and all fibers were conditioned prior their first use (1h at 220 °C) and cleaned during 10 min before their daily use. A Trace 1300 gas chromatograph equipped with a flame ionization detector (FID) was used to separate and analyze the extracted fraction. The GC injector was kept at 220 °C with a splitless time of 3 min and FID was kept at 250 °C. A Trace TR-V1

(30 m x 0.250 mm x 1.40 μm) capillary column from Thermo Scientific was used with the following temperature program: initial temperature of 50 $^{\circ}\text{C}$ during 1 min, followed by a ramp at 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 80 $^{\circ}\text{C}$, held during 5 min and then increased to 250 $^{\circ}\text{C}$ at a ramp of 50 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

2.5 Analytical performance evaluation

The analytical performance of the prepared fibers was evaluated performing SPME extractions in the following conditions: for *Alcohols* - $T = 45^{\circ}\text{C}$, $t = 15$ min and 20 wt. % of NaCl, using standard aqueous solution concentrations varying from 40 to 1000 $\mu\text{g}\cdot\text{L}^{-1}$; for *BTEX*: $T = 45^{\circ}\text{C}$, $t = 10$ min and 2 wt. % of NaCl, using standard solution concentrations varying from 0.35 to 200 $\mu\text{g}\cdot\text{L}^{-1}$. Linearity was studied in the same range of concentrations for all the analytes using the optimized conditions and the limits of detection (LOD) were determined by decreasing the concentration of the standard solution until the signal to noise ratio (S/N) of 3 was attained.

3. Results and discussion

3.1 Synthesis of poly(ionic liquids)

The facile procedure used for the synthesis of poly(Pyrr₁₁ TFSI) is well established in the literature [29,30] and was accomplished by the anion exchange reaction of the commercially available poly(Pyrr₁₁ Cl) using LiTFSI, since [TFSI] anion is known for its high thermal stability [29,30]. By using a hydrophobic anion, such as [TFSI], the former aqueous soluble polymer is readily precipitated in the form of poly(Pyrr₁₁ TFSI) and thus, only one purification step to wash the resulting material from the excess of salts in solution is needed. In the end, a material with controlled properties, such as molar mass, excellent thermal and mechanical properties is easily

obtained. Despite our recent report on poly(diallylalkylammonium TFSI) as SPME fibers [18], poly(Pyrr₁₁ TFSI) was never used in SPME. However, its high thermal stability, between 400 and 500 °C [29], makes it an excellent candidate for SPME phase since the usual working temperatures of both extraction and desorption temperatures do not exceed 350 °C.

On the other hand, the synthesis of a specific IL monomer allows for the fine chemical tuning of the polymer to meet specific application needs. Poly(ViBnIm-co-Sty Br), was synthesized through RAFT polymerization with styrene and a vinylimidazolium monomer containing a benzyl as pendant group ([ViBnIm]Br). The TFSI based polymer was obtained by simple metathesis reaction, using LiTFSI salt. From the ¹H and ¹³C NMR data of [ViBnIm]Br and also poly(ViBnIm-co-Sty TFSI) presented in supporting information Figure S1 to S3, the synthesis of both monomer and polymer were successfully achieved. Regarding the thermal properties of both copolymers, poly(ViBnIm-co-Sty Br) and poly(ViBnIm-co-Sty TFSI) showed decomposition temperatures higher than 275 °C, as can be seen on Figures S4 and S5 of supporting information. From differential scanning calorimetry (DSC) (Figures S6 and S7), poly(ViBnIm-co-Sty Br) and poly(ViBnIm-co-Sty TFSI) showed glass transition temperatures of 69 °C and 63 °C, respectively. This very small difference can be attributed to the asymmetric nature of the [TFSI]⁻ anion, lowering the glass transition of the polymer. These glass transition values mean that the SPME extraction step (if up to 63 or 69 °C) will be performed with a vitreous-state coating phase, while the desorption step (normally performed at temperatures higher than 200 °C) will be accomplished with the material in rubbery-state. Although both polymers are suitable as SPME coating phases, the presence of a glass transition temperature can have great impact on

the analytes mass transfer, from the matrix headspace to the coating phase and from this to the GC injector.

3.2 Fiber coating

For the preparation of the SPME fiber coatings the synthesized polymers were firstly grinded using an electrical coffee grinder. This procedure allowed to obtain fine particles that were later used in the production of the SPME coating phases. The distribution size of the polymeric particles obtained after 2 min of grinding is shown in Figure 2a. It can be observed that 85 % of the particles have diameters between 2 and 10 μm and from these, 56 % have sizes between 4 and 8 μm . These particles with heterogeneous sizes were used in the preparation of the fiber coatings using poly(Pyrr₁₁TFSI) (Fiber: PyrrTFSI), poly(ViBnIm-co-Sty Br) (Fiber: VBSBr) and poly(ViBnIm-co-Sty TFSI) (Fiber: VBSTFSI).

To attach the grinded polymers to the steel wire, a solution of silicon adhesive dissolved in toluene was used as binding agent. The steel wire was vertically inserted in the prepared solution and slowly retracted creating a coating of silicon adhesive. Afterwards, it was possible to attach the PIL particles to the steel support by rotating it over the polymeric grinded particles, as shown in Figure 2b. In Figure 2c and 2d, the SEM images of the bare steel wire and VBSBr PIL coated fiber are presented respectively. The particles create a rough surface (Figure 2d and Figure S8 of supporting information) thus enhancing the surface area between the extraction phase and the analytes. The average thickness of the prepared extraction phases of these PIL particles coating configuration was $19 \pm 4 \mu\text{m}$.

3.3 Optimization of headspace-SPME parameters

To obtain the best extraction efficiency, different experimental parameters that affect extraction efficiency such as salt addition, extraction time, extraction temperature, or desorption temperature were optimized for both standard solutions of BTEX and alcohols using the VBSBr fiber. This fiber was chosen as model due to the presence of aromatic moieties in the cation that have chemical similarity for the BTEX mixture and also due to the hydrogen basicity of the anion that is suitable for polar compounds. The optimization conditions obtained for this specific fiber coating were used for the remaining fibers, although keeping in mind that every fiber coating can have slightly different optimal conditions. The extraction parameters optimized for the alcohol and BTEX aqueous solutions, respectively, for VBSBr fiber are shown in the Figure S9 and S10.

3.3.1 Sorption time

The effect of the extraction time was accessed in terms of peak areas by varying the extraction time from 5 min to 30 min. As can be seen in Figure S9a, the highest extraction was obtained at 15 min and remained almost constant until 30 min. This short extraction time can be attributed to the high surface area of the prepared PIL particles fiber coatings, leading to fast adsorption and desorption of analytes [31]. At 7.5 min, more than 85% of the maximum extraction efficiency was obtained, confirming the importance of the high surface area in the extraction times. Regarding BTEX aqueous solutions, it was also observed that these fibers achieve high extraction efficiency at 10 min, being the highest extraction efficiency obtained at 15 min (Figure S10a). In summary, 15 min was chosen as the optimal extraction time.

3.3.2 Extraction temperature

Temperature plays a key role in the efficiency of HS-SPME and its influence was studied from 25 °C to 55 °C. After 55 °C, water starts to be an impurity that can influence the mass-transfer rate and therefore, no higher temperatures were studied. For the alcohols aqueous solutions, an increase in temperature up to 45 °C leads to an increase in the extraction efficiency, while at higher temperatures it starts to decrease (Figure S9b). For BTEX mixture, 45 °C was also found to be the best extraction temperature, resulting in higher efficiency (Figure S10b).

3.3.3 Desorption temperature

The influence of desorption temperature in extraction efficiency of both families of analytes was studied from 200 °C to 240 °C, using a 3 min desorption time. The extraction efficiency does not vary considerably in the studied range regarding headspace extraction of alcohols (Figure S9c). For the BTEX extraction, an increase in the extraction efficiency is observed up to 220 °C. Therefore, 220 °C was the desorption temperature used in our studies.

3.3.4 Salt addition

The salting-out effect is particularly important when dealing with HS-SPME [5]. The addition of salting-out inducing agents, such as NaCl, to the aqueous solutions can improve its efficiency. The influence of NaCl on the extraction efficiency was studied from 0 % up to 30 wt. % of NaCl. For the alcohols extraction, the addition of 20 wt. % of NaCl increased 50 % the extraction efficiency. For higher salt concentrations, no significant effect was observed (Figure S9d). Regarding BTEX aqueous solutions, the addition of 2 wt.% of NaCl improved the extraction efficiency. However, higher

concentration of NaCl unexpectedly decreased the extraction performance (Figure S10d). This somewhat unexpected behavior was already reported in various other works in this area [32–35], therefore we herein used 2 wt.% of NaCl for BTEX mixture and 20 wt.% of NaCl for the alcohol mixture.

3.4 Performance of the prepared fibers

Once the optimal parameters were defined for both sets of analytes, the extraction efficiency of PIL based fibers was examined by comparing the peak areas obtained for the model analytes of alcohols and BTEX with those obtained by commercial fibers and they are presented in Figure 3. On both cases, the silicon used to attach the PIL particles was also tested alone and—as can be seen, no relevant sorption was detected.

The three PIL based fibers showed higher extraction efficiency compared with PDMS and PA commercial fibers. As the sample sorption is governed by absorption mechanism in all fibers, the high contact area obtained by the PIL particles based fibers contributes to a higher sensitivity. To confirm this, a fiber containing a homogeneous film coating (VBSTFSI-F) was prepared using spray-coating [17], and as can be seen in Figure 3, the PIL particles based fibers showed higher extraction efficiencies.

Among the three PIL particles based fibers, VBSBr and VBSTFSI showed overall high extraction efficiency for the alcohols mixture, being ethanol, butanol and benzyl alcohol the most extracted analytes. The extraction capability of these more hydrophilic (low log K_{ow}) and polar analytes (Table S1) can be explained by the different polarity of the PILs polycations. The presence of two nitrogen atoms in poly(ViBnIm-co-Sty X) polycations (X = Br or [TFSI]) and their aromatic character contrasts with one nitrogen and non-aromatic character of poly(Pyrr₁₁ TFSI), that is in

line with analogue ILs behavior [36,37]. Moreover, the acidic proton from the carbon 2 between both nitrogen atoms of the imidazole ring favors the interaction with the hydroxyl group of the alcohol analytes making these two fibers more efficient for these polar analytes. Between the VBSBr and VBSTFSI fibers, the former showed the highest extraction efficiency due to the presence of the bromide anion that is able to undergo hydrogen bond interactions with the polar analytes [25,38]. Additionally, the importance of the chemical tunability of PILs is clearly shown by the high extraction efficiency observed for benzyl alcohol that was efficiently extracted with the PIL particle fibers rather than with the commercial fibers. This is justified by the presence of aromatic moieties in VBSBr and VBSTFSI that leads to an increase of π - π interactions and, consequently, a large chemical affinity between fiber coating and analyte.

Concerning the extraction of the BTEX compounds, PyrrTFSI shows similar extraction efficiency in terms of total detected peak areas with PDMS, with PyrrTFSI extracting benzene and xylene slightly better than PDMS. The hydrophobic nature of the anion and cation, together with the lack of aromaticity in the PyrrTFSI fiber leads to an extraction mechanism involving mostly weak van der Waals forces. On the other hand, the VBSBr and VBSTFSI fibers showed the highest extraction efficiency, which can be attributed to the strong π - π interactions between these two fibers and the analytes. The presence of aromatic benzyl groups in the imidazolium rings of the polycations, but also the styrene repeating unit largely contributes to these interactions. Furthermore, VBSTFSI showed a slightly higher extraction efficiency that can be explained by the [TFSI] anion, that confers a more hydrophobic nature to the polymer, resulting in higher extraction capability of non-polar compounds.

3.5 Analytical performance evaluation

The calibration parameters, limits of detection, relative standard deviations (RSD) and reproducibility from fiber to fiber (Rep F2F) are shown in Table 1 for all studied compounds. Good correlation factors were obtained in all samples with RSD between 6.0 and 16.2 %. The reproducibility from fiber to fiber was found by comparing extractions performed in different days with different fibers and lead to differences between 10.4 and 22.5 %, which can be attributed to the different particle sizes. The detection limits are shown in the aforementioned Table 1 and they were determined by decreasing the concentration of the samples until a signal to noise ratio of 3:1. The LODs obtained for ethanol and butanol are lower than those obtained using PA and PDMS/DVB fibers [26] and the comparison with other PIL based fibers is listed in Table 1 showing the potential in using PIL based phases.

4. Conclusions

In this work, three poly(ionic liquids), poly(Pyrr₁₁ TFSI), poly(ViBnIm-co-Sty Br) and poly(ViBnIm-co-Sty TFSI), were used to prepare SPME phases to extract polar and aromatic compounds. The fibers were successfully fabricated using a quick and simple method to achieve high superficial area for better extraction performance. Moreover, poly(Pyrr₁₁ TFSI) was used for the first time as a SPME extraction phase and revealed extraction performances comparable or even superior with the commercial fibers. However, the best performance was achieved for the fibers composed of poly(ViBnIm-co-Sty Br) and poly(ViBnIm-co-Sty TFSI) for both polar and aromatic compounds. Depending on the polarity of the analytes, this work showed that the right choice of PIL counter anion influences the overall extraction efficiency, with the bromide anion, having strong hydrogen bond ability is suited for polar analytes and a

more hydrophobic anion such as [TFSI] suitable for nonpolar analytes. The work also demonstrates the important advantage of PILs chemical tunability through the increased extraction efficiency of polymers containing aromatic moieties in their structure, thus achieving an optimal chemical selectivity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://xxx>

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Figure 1. Preparation of: a) poly(ViBnIm-co-Sty TFSI) and b) poly(diallyldimethylammonium TFSI).

Figure 2. Representation of a) poly(ViBnIm-co-Sty Br) particle size distribution percentage and b) the overall fiber fabrication. SEM images of: c) bare steel wire at 140X magnification; d) VBSBr fiber at 140x magnification and e) the same VBSBr fiber at 16x magnification.

Figure 3.a) Performance of all the studied fibers in the alcohols aqueous mixture at $T = 45^{\circ}\text{C}$, $t = 15$ min, concentration = $500\ \mu\text{g}\cdot\text{mL}^{-1}$, 20 wt. % of NaCl and a desorption temperature of 220°C ; b) Performance of all the studied fibers in an BTEX aqueous mixture studied at $T = 45^{\circ}\text{C}$, $t = 15$ min, concentration = $100\ \mu\text{g}\cdot\text{mL}^{-1}$, 2 wt. % of NaCl and a desorption temperature of 220°C .

Table 1 – Analytical performance of the VBSBr fiber under optimized conditions for alcohols and BTEX.

Compound	Linear range $\mu\text{g}\cdot\text{L}^{-1}$	R	slope	LOD $\mu\text{g}\cdot\text{L}^{-1}$ (S/N=3)	RSD %	Rep F2F %	LOD other PILs $\mu\text{g}\cdot\text{L}^{-1}$
Ethanol	40-1000	0.9987	83 ± 0.9	2.20	16.2	22.5	15[26]; 0.02[39]; 20[24]
1-Butanol	40-1000	0.9996	179 ± 12	1.32	13.1	17.8	7[26]; 0.005[39]
2-Heptanol	40-1000	0.9993	457 ± 43	0.91	12.9	13.5	5[18]
Benzyl alcohol	40-1000	0.9997	87 ± 9.4	0.19	10.7	16.2	20[18]
1-Octanol	40-1000	0.9994	354 ± 13.9	0.11	7.5	12.2	0.4-6[40]; 0.09;0.07[41]
Benzene	0.35-200	0.9986	11215 ± 131.9	0.06	6.0	13.4	200[14]; 0.05[42];
Toluene	0.35-200	0.9985	13183 ± 112.6	0.04	8.2	14.5	100[14]; 0.03[42];
Ethylbenzene	0.35-200	0.9992	7243 ± 31.9	0.02	6.9	10.4	800[14]; 0.02[42];
Xylene	0.35-200	0.9993	6343 ± 102.2	0.02	8.9	11.7	800[14]; 0.02[42]; 0.1- 8[40];

Highlights

- PIL co-polymers embedded particles were used as heterogeneous SPME fibers.
- Fast and easy fiber preparation through PILs grinding and gluing to steel.
- The prepared fibers showed high affinity for alcohols and BTEX mixtures.
- PILs tunability achieved with the introduction of aromatic and polar moieties.
- Higher extraction efficiency than commercial PDMS and PA fibers.

Figure 1.

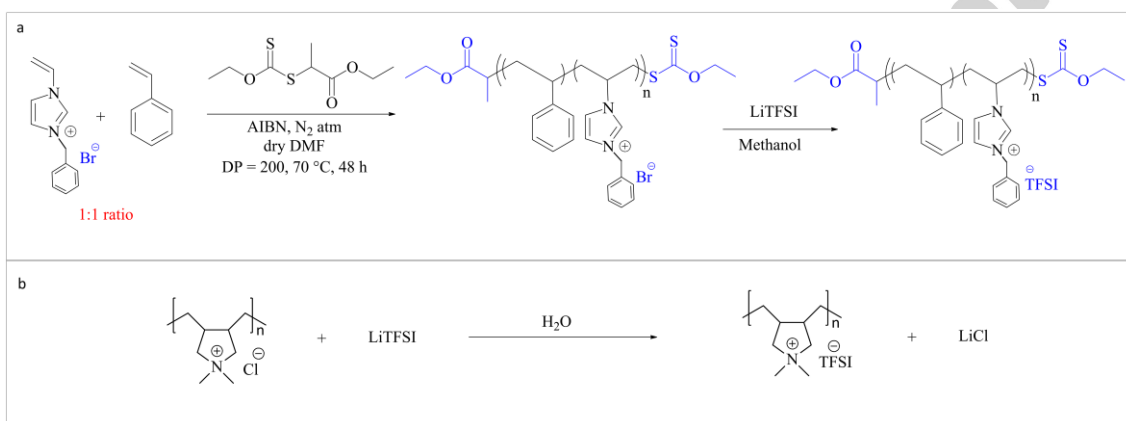


Figure 2.

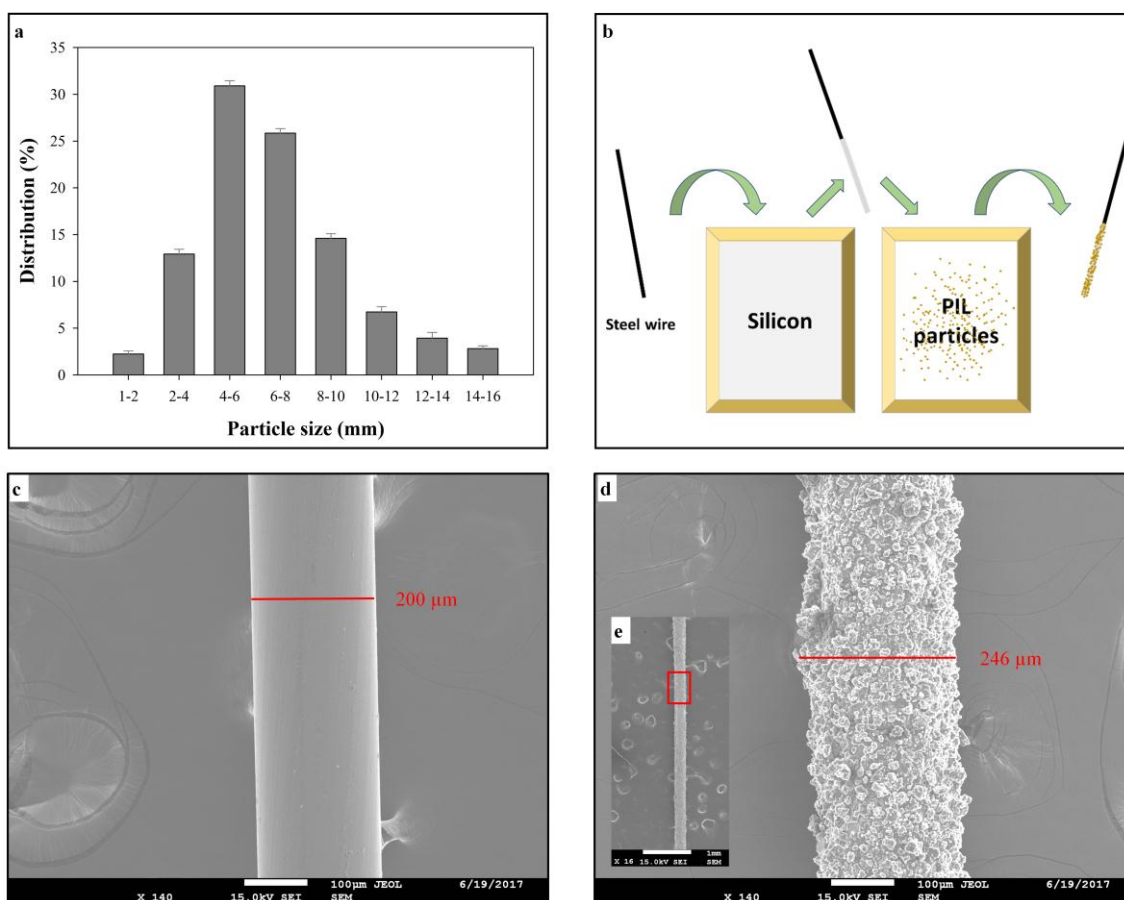


Figure 3

