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Samuel Carda-Broch[a]; Maria Jose Ruiz-Angel[b]; Daniel W. Armstrong[c]; Alain Berthod[d]
[a] Departament de Química Física i Analítica, Universitat Jaume I, Castelló, Spain [b] Departament de Química Analítica, Universitat de València, c/Dr. Moliner, Burjassot, Spain [c] Department of Chemistry, University of Texas - Arlington, Arlington, Texas, USA [d] Laboratoire des Sciences Analytiques, Université de Lyon, CNRS, Villeurbanne, France

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Ionic Liquid Based Headspace Solid-Phase Microextraction-Gas Chromatography for the Determination of Volatile Polar Organic Compounds

Samuel Carda-Broch,[1] Maria Jose Ruiz-Angel,[2] Daniel W. Armstrong,[3] and Alain Berthod[4]

[1]*Departament de Química Física i Analítica, Universitat Jaume I, Castelló, Spain*
[2]*Departament de Química Analítica, Universitat de València, c/Dr. Moliner, Burjassot, Spain*
[3]*Department of Chemistry, University of Texas – Arlington, Arlington, Texas, USA*
[4]*Laboratoire des Sciences Analytiques, Université de Lyon, CNRS, Villeurbanne, France*

Solid-phase microextraction (SPME) with an ionic liquid (IL) coating was developed for headspace extraction of a group of low molecular weight alcohols (ethanol, n-propanol, butanol, and isopropyl alcohol), acetone, ethyl acetate, and acetonitrile. A first SPME fiber was simply coated with a dedicated IL whose synthesis is described. A second SPME fiber was prepared by gluing silica (Si) particles on which the synthesized IL was chemically bonded. The analytes SPME extraction was optimized for time, temperature, and NaCl salting out content. The headspace extracted analytes were determined by simple temperature desorption into the hot injection port of a gas chromatograph. The coated-IL fiber did not have enough extracting material to be useful. The bonded-IL-Si particle fiber had much more extracting material. Its analytical capabilities were compared to those of two commercially available fibers. The extraction yields of the bonded-IL-Si fiber were inferior to those of the two commercial fibers because they contained a significantly higher amount of extracting material. The linear concentration range could reach up to 120 µg/mL. The recoveries, trueness, and precision (RSD) were in the 97.4–109.5%, 0.1–9.5%, and 0.7–16.5 ranges, respectively. The bonded-IL-Si fiber showed a specific affinity for ethanol giving an ethanol peak height equal or greater than that of the two commercial fibers tested with the same sample.

Keywords gas chromatography; headspace extraction; ionic liquid; polar compounds; SPME

INTRODUCTION

The development of an analytical method frequently involves working with complex matrices of a different nature. The complexity of the sample may impose adaptations of the extraction and/or separation technique. Often the complete recovery of the desired analyte is limited; part of it staying with matrix components. Solid-phase microextraction (SPME) is a relatively new type of sample preparation technique that offers several advantages over other traditional extraction procedures (e.g., Soxhlet extraction or liquid-liquid extraction). Developed by Pawliszyn and co-workers in the early 1990s (1,2), SPME is a solvent-free method that integrates extraction, concentration, and sample clean up in one step, and can be easily coupled with different analytical instruments, especially gas chromatography (GC).

SPME devices incorporate an extraction fiber, usually made of a fused silica fiber or metal wire with an extraction coating (3). The fiber is exposed to the sample using either the headspace or direct-immersion protocols. Once the equilibrium between analyte(s) and coating material is established, desorption from the fiber coating can take place. When GC is the analytical technique used, analyte thermal desorption is directly achieved by exposing the SPME fiber to the hot injection port of the chromatographic system (4–7).

Different types of fibers have been commercialized. Among them, polydimethylsiloxane (PDMS) or polyacrylate (PA) coatings are widely used. They show excellent selectivities for non-polar and relatively polar analytes, respectively. Nevertheless, several limitations related to limited life span, relatively low operating temperatures in GC (200–270°C), and variable performance of the fiber depending on the manufacturer have been addressed. This affects the selectivity and sensitivity of the extractions. In order to overcome these drawbacks new coating materials, such as ionic liquids (ILs) have recently attracted some attention. ILs are salts that exhibit low melting points and negligible vapor pressure (8). A large number of different cations and anions can be associated to form ILs. A specific IL can be custom-designed for a specific task. Their low volatility and relatively high and adjustable polarity make them potential candidate new sorbents in SPME

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Address correspondence to Alain Berthod, Laboratoire des Sciences Analytiques, Université de Lyon, CNRS, Bat CPE, 69622 Villeurbanne, France. Tel.: +33 472 448 296. E-mail: berthod@univ-lyon1.fr

fibers. Several IL-based SPME methods have been reported in the literature (9–12). All reports describe fiber preparations that are time-consuming and poorly reproducible (9,10). Recently, the thermal stability, reproducibility, and the life-time of new original IL coatings have been developed by using polymeric ILs (11,12), but improvements are still needed.

In the present study, different ILs were attached to fibers that were used for SPME extractions. Polar compounds such as low molecular weight alcohols (ethanol, n-propanol, butanol, and isopropyl alcohol), acetone, ethyl acetate, and acetonitrile were targeted as solutes difficult to extract with commercially available SPME fibers. These polar volatile compounds may arise in waste waters and are also of interest in forensic (arsons) and clinical analyses for rapid sobriety assessment. Extraction with the prepared IL coating was optimized and compared with commercial and other IL-based fibers.

MATERIAL AND METHODS

Reagents

Standard stock solutions of acetone, acetonitrile, butanol, ethanol, ethyl acetate, isopropyl alcohol, and propanol, all supplied by Sigma-Aldrich (L'Isles d'Abeau Chesnes, France), were prepared by dissolving 0.1 mL of each individual compound in water. These solutions were stored refrigerated at 4°C. Working solutions were prepared daily by diluting the stock solutions at the appropriate concentration (15 µg/mL, approximately). NaCl was supplied by JT Baker (Mallinckrodt, Phillipsburg, NJ, USA). Ultrapure water was obtained from a Barnstead (Thermo Scientific, Courtaboeuf, France) and used throughout.

The reagents imidazole, 1-methylimidazole, 1-hydroxyethyl imidazole, triethylene glycol, phosphorous tribromide, ethyl acetate, toluene, 4-vinyl chlorotoluene, tetrahydrofurane (THF), *n*-butanol, methylene chloride, chloroform, dioxane, butyric acid, phenol, dimethylamine, trimethylamine, pyridine, and aniline were purchased from Sigma-Aldrich. Kromasil spherical silica gel with 5 µm particle diameter, 10 nm pore size, and 310 m^2/g surface area was obtained from Supelco (Sigma-Aldrich, Bellefonte, PA, USA).

Apparatus and Equipment

All extractions were done using the headspace procedure. The Supelco SPME fiber assembly was used with a holder 57330 and a 57357-U stand with heater block holding up to eight 4 mL vials (Supelco). A Corning PC420-D heater/magnetic stirrer plate was used to maintain the vials at 50°C during the headspace extraction time.

All analyses were carried out using an Agilent gas chromatograph (Palo Alto, CA, USA) equipped with split–splitless injector and flame ionization detector (FID). Separations were performed using a polyoxyethylenglycol fused-silica column (Carbowax 20 M, 30 m × 250 µm × 0.25 µm) from Supelco. The column oven temperature was programmed as follows: initial temperature of 40°C for 3 min, then rising to 140°C at a rate of 10°C/min and hold for 5 min, and finally decreased to 40°C at a rate 15°C/min. The injector port was operated with splitless mode at 120°C, while the detector temperature was maintained at 300°C. High purity helium was used as carrier gas (1.0 mL/min). Hydrogen and air were used as detector gases at 40 mL/min and 450 mL/min, respectively. The signal from the FID was monitored and processed by a Chemstation chromatographic integration software (Agilent, Santa Clara, CA, USA).

Ionic Liquid Synthesis

The first ionic liquid synthesized contained polar oxyethylene units and imidazolium rings. Bis-hydroxyethyl imidazolium trioxyethylene dibromide was synthesized as previously described (13). Simply, trioxyethylene dibromide was reacted at 80°C under reflux for 12 hours with hydroxyethyl imidazole, in an exact one to two molar ratio. The bromide imidizolium salt obtained was solid at room temperature. It was reacted with lithium bis(trifluoromethyl sulfyl)amide (Li NTf_2) in dry methanol to obtain the corresponding bis-triflyl imidazolium ionic liquid coded IL1 (Fig. 1). The same procedure was done using lithium trifluoromethyl sulfate (Li TfO) to form the triflate imidazolium ionic liquid coded IL2 (Fig. 1). IL1 and IL2 were directly used to coat SPME fibers.

IL1 and IL2 were also further modified to be bonded to spherical silica particles that were glued on SPME fibers. The two ILs were reacted in acetonitrile with triethoxysilane ethylisocyanate in an equimolar ratio for four hours at room temperature. The carbamate linked IL-triethoxysilanes obtained were reacted with half their weight of 5 µm Kromasil spherical silica particles. The Fig. 1 (bottom)

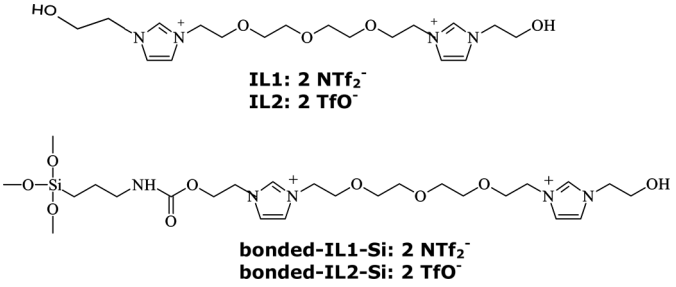

FIG. 1. Top: Structures of the ionic liquids coated on SPME fibers; IL1 is the bis-triflylamide salt and IL2 is the triflate salt of the same bis-hydroxyethyl imidazolium trioxyethylene cation. Bottom: the cations were bonded via a carbamate link to silica particles that were glued on SPME fibers, according to the associated anions, bonded-IL1-Si and bonded-IL2-Si particles were obtained.

bonded structure was obtained. The C, H, and N elemental analysis percentages for the bonded silica particles were respectively 9.18%, 1.47%, and 2.48% with the NTf_2 IL1 of molecular weight 1087 allowing estimating the bonding silica density as 1.2 μmol/m^2. The respective values for the TfO IL2 were 8.41%, 1.32%, and 2.05%. The 819 m.w. of the grafted IL produces a similar 1.1 μmol/m^2 bonding density for the second IL bonded material.

Fiber Preparation

The synthesized ionic liquids IL1 and IL2 were sent to Supelco that used its usual proprietary procedure to coat porous silica SPME fibers. These two fibers are referred to as coated-IL1 and coated-IL2 fibers. The IL bonded silica particles were also sent to Supelco that glued them onto a SPME flexible metallic wire that fitted the fiber holder exactly. A proprietary protocol was specially designed to obtain a glued thickness layer of about 50 μm (Supelco, Sigma-Aldrich Group). The Supelco company did not provide nor authorize the disclosure of any more information concerning the fiber preparation. The two fibers with glued silica particles are referred to as bonded-IL1-Si and bonded-IL2-Si fibers.

Method

A classical headspace SPME procedure was adopted. Solid NaCl was added to the aqueous sample solution to produce a salting-out effect and enhance the volatile compound concentration in the vapor phase. NaCl was weighed and transferred to a 4 mL headspace glass vial. After adding a micro-stirring bar, 2.5 mL of the working solution containing the target analytes were also added. The vial was sealed, slightly mixed, and placed on top of the Corning magnetic hot plate at a constant stirring rate of 900 rpm and temperature 50°C. Next, the SPME fiber holder was used to expose the fiber to the vapor phase in the headspace of the vial. After the extraction, the fiber was retracted in the holder. It was immediately analyzed by inserting the holder into the GC port and exposing the fiber at 120°C for thermal desorption of the extracted analytes into the GC injector in splitless mode. The fiber desorption time was kept at 3 min for all experiments. Two commercial SPME fibers employing a polydimethylsiloxane/divinylbenzene (PDMS/DVB) and polyacrilate (PA) coatings with a film thickness of 100 and 85 μm, respectively (Supelco) were also used. These commercial fibers were conditioned at 250°C for 2 h in the injection port of the gas chromatograph according to the manufacturer's instructions.

RESULTS AND DISCUSSION

Comparing the Four Different Fibers

The coated and particle bonded ionic liquid fibers were compared together by extracting the same synthetic sample solution using exactly the same experimental conditions. A 15 μg/mL solution of acetone, ethyl acetate, isopropanol, ethanol, acetonitrile, 1-propanol, and 1-butanol was prepared and the headspace extracted by the four fibers. Figure 2 shows the four chromatograms. The two fibers, bonded-IL1-Si and bonded-IL2-Si, with glued IL bonded silica particles (Fig. 2c and d) are clearly better in terms of peak height and area as well as peak shapes than the two coated IL1 and coated-IL2 fibers (Figs. 2a and b). In terms of peak heights, the coated-IL1 fiber produced peak heights (Fig. 2a) from 40% to 70% lower than the bonded-IL1-Si particle fiber peak heights (Fig. 2c). A similar observation can be made between the coated-IL2 fiber (Fig. 2b) and the bonded-IL2-Si fiber (Fig. 2d). In both cases, IL1, with the bis-triflyl amide anions, gave superior results compared to IL2 with triflate anions. Considering these results, the rest of the study was done with the (bis-triflyl anionic) bonded-IL1-Si SPME fiber exclusively.

Optimization of Extraction Parameters

The newly developed bonded-IL1-Si fiber was applied to determine different target analytes in water in different conditions. Three important factors influencing the headspace liquid-gas analyte equilibrium are: the extraction temperature, extraction time, and salting out effect in terms of salt concentration. These three parameters were investigated in order to maximize the analyte extraction efficiency with the bonded-IL1-Si fiber.

The extraction temperature has an important effect on headspace SPME. An increase of temperature increases the headspace vapor pressure of all compounds favoring the volatile compound concentration in the gas phase. It also enhances the diffusion coefficients of the analytes in the gas phase, which increases the extraction rate. However, it also decreases the amount of analytes that can concentrate in the fiber coating. The effect of temperature on the extraction of the analytes was investigated in the 0–60°C range. Figure 3 (left) shows the analyte peak areas plotted versus the extraction temperature from 20°C to 60°C for a sample solution containing approximately 5 μg/mL of volatile analytes and extracted for 5 min. The experiments done below room temperature were poorly reproducible with very low extracted amounts. The peak areas increased from 0°C to 40°C approximately, and then reached a plateau with almost no change between 50°C and 60°C. Therefore, 50°C was adopted as the optimum temperature for all following SPME experiments.

In order to obtain stable responses and allow the analytes to reach equilibrium, the extraction time must be long enough. It was optimized in the range 2–30 min. As shown in Fig. 3 (right), the peak areas of analytes increased significantly over the first 10 min and then the gain in concentration was less significant even with prolonged extraction

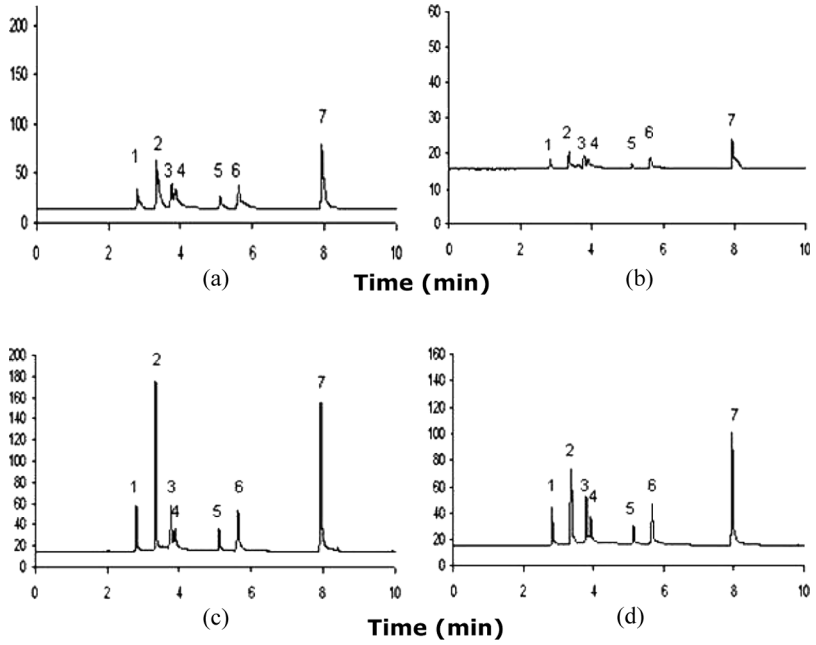

FIG. 2. Gas chromatograms obtained with: (a) coated-IL1 and (b) coated-IL2 SPME fibers, (c) bonded-IL1-Si and (d) bonded-IL2-Si fibers with silica particles glued on SPME fibers. Compounds: (1) acetone, (2) ethyl acetate, (3) isopropyl alcohol, (4) ethanol, (5) acetonitrile, (6) propanol and (7) butanol, 15 μg/mL each. Column Carbowax 20 M (30 m × 250 μm × 0.25 μm), initial temperature 40°C hold for 3 min (splitless time), followed by a temperature ramp of 10°C/min for 10 min to 140°C. Carrier gas helium, 1 mL/min, split ratio 20/1. Extraction conditions: 10 min at 50°C with 30% w/v salting-out NaCl added to the aqueous solution.

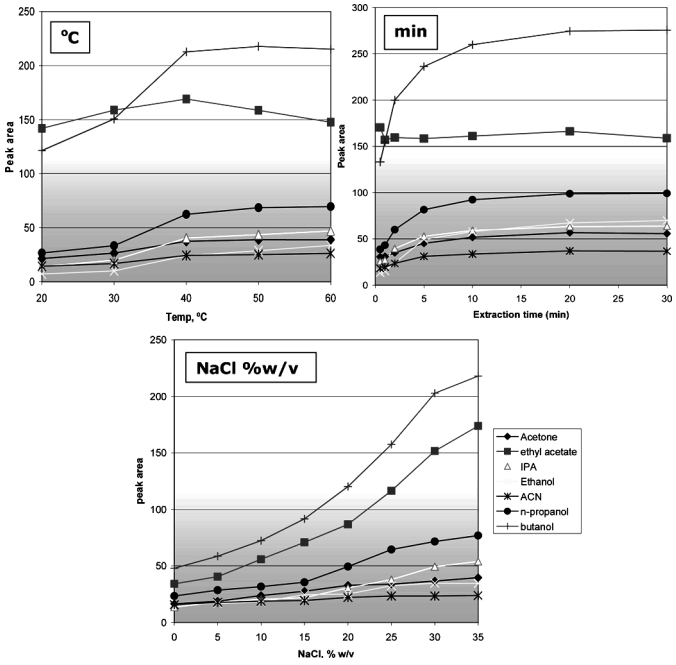

FIG. 3. Optimization of the bonded-IL1-Si SPME fiber extraction. The temperature study was done with 30% w/v salt content and 5 min extraction time. The extraction time study was done at 50°C temperature and 30% w/v added salt. The salt effect study was done at 50°C temperature and 5 min extraction time. Analyte concentration: 5 μg/L each.

times. The same trend was observed for all studied analytes. Reasonable compromise concentration/experiment duration of 10 min was selected. This 10 min extraction time was used for all further extractions. Ethyl acetate shows a different behavior versus extraction time (Fig. 3, right). This compound equilibrates much faster than the other tested compounds that were all alcohols with H-bond possible interactions and acetonitrile, a small polar molecule. Ethyl acetate as well as acetone (also less sensitive to equilibration time) are less polar compounds able to establish their liquid-gas equilibrium faster than alcohols.

The addition of an inorganic salt to a sample solution is a usual practice that improves extraction efficiency for volatile compounds by salting them out of the aqueous solution. For many compounds, a high salt concentration decreases their solubility in the aqueous phase and thus increases their vapor pressure in the headspace. With this purpose, the influence of NaCl on the studied system was investigated. The NaCl concentration varied from 0% w/v (or 0 g/L) to 35% w/v (or 350 g/L). 350 g/L NaCl is the saturation concentration at 50°C. At 20°C, the saturation concentration is only 316 g/L. The salt-out effect is shown in Fig. 3 (bottom). As more salt is added, more solute are extracted by the SPME fiber. To reduce salt precipitation, the selected salt concentration for further analyses was 300 g/L or 30% w/v NaCl.

Bonded-IL1-Si Fiber versus Commercial PDMS/DVB and PA Fibers

The bonded-IL1-Si based fiber was compared with a 100 μm commercial polydimethylsiloxane/divinylbenzene (PDMS/DVB) and a 85 μm polyacrylate (PA) fibers. These two commercial coatings are considered to facilitate the extraction of relatively polar analytes. The optimal conditions previously established for the bonded-IL1-Si fiber were also used for the two PDMS/DVB and PA fibers. However, according to the manufacturer's instructions, the temperature of the GC injection port was set at 250°C and the column oven temperature program was raised to 180°C instead of 140°C.

Figure 4 depicts the chromatograms obtained with bonded-IL1-Si, PDMS/DVB and PA fibers for a sample solution containing 15 μg/mL of each analyte. It can be observed that the PDMS/DVB fiber was clearly superior to the bonded-IL1-Si fiber for the extraction of ethyl acetate, propanol and butanol and somewhat better for acetone and isopropyl alcohol. The PA fiber gave somewhat higher peak areas for the ethyl acetate and butanol analytes only. For the other compounds, the peak areas were similar in both cases. The low bonding density (1.2 μmol/m^2) of IL1 on silica particle associated to a possible low thickness layer (or mass of adsorbing material) of the bonded-IL1-Si fiber are the most probable reason for the lower performances of the newly developed fiber compared to those of the optimized commercial fibers. However, the bonded-IL1-Si fiber had relatively acceptable extraction efficiency for ethanol compared to both PA and PDMS/DVB.

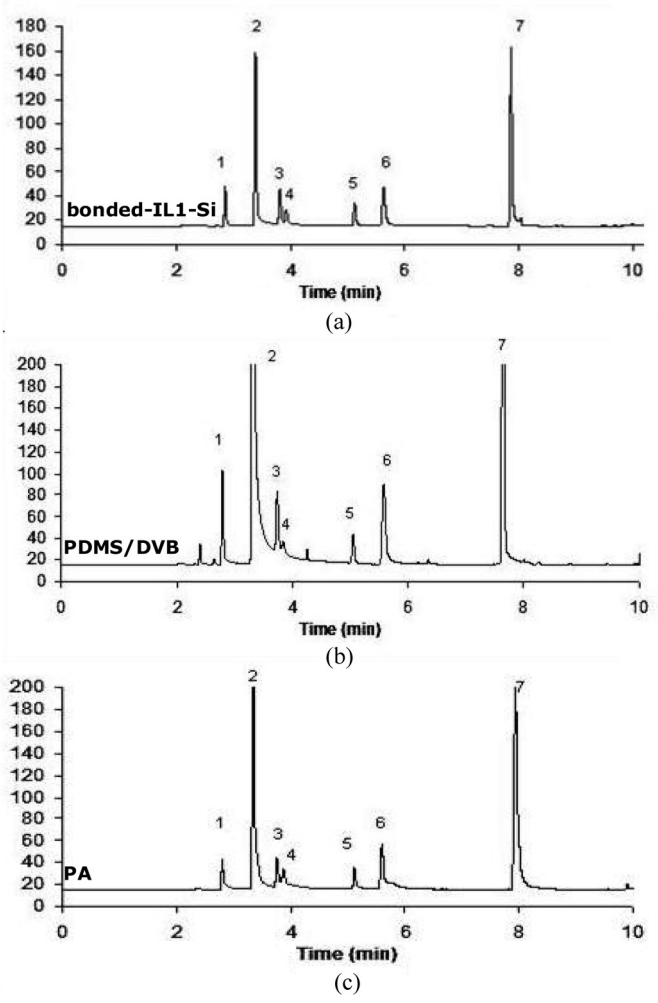

FIG. 4. Chromatograms obtained with: (a) bonded-IL1-Si fiber, (b) PDMS/DVB and (c) PA commercial fibers and headspace extraction of the same synthetic mixture. Compounds: (1) acetone, (2) ethyl acetate, (3) isopropyl alcohol, (4) ethanol, (5) acetonitrile, (6) propanol and (7) butanol, 15 μg/L each. Chromatographic and extraction conditions: see Fig. 2 caption.

Figure 5 plots the results obtained in terms of sensitivity, expressed as solute GC peak area per μg/mL, versus the solute hydrophobicity expressed as its log $K_{o/w}$. There is a clear relationship between the amount extracted by all four fibers and the solute hydrophobicity. Acetonitrile (log $K_{o/w} = 0.474$) is clearly out of trend, probably due to its high volatility. The combination of these results seems to indicate that the bonded-IL1-Si fiber is somewhat more effective for the extraction of very low molecular weight polar compounds while PDMS/DVB and PA fibers would be more appropriate as the molecular size and hydrophobicity increases. The PDMS/DVB fiber is the best of the three in terms of the global peak area. It should, however, be noted that it is also the fiber with the thicker coating (100 μm) compared to the 85 μm of the PA fiber and 50 μm of the bonded-IL1-Si fiber. It is likely that a higher adsorbent volume allows for a better adsorption of the solutes.

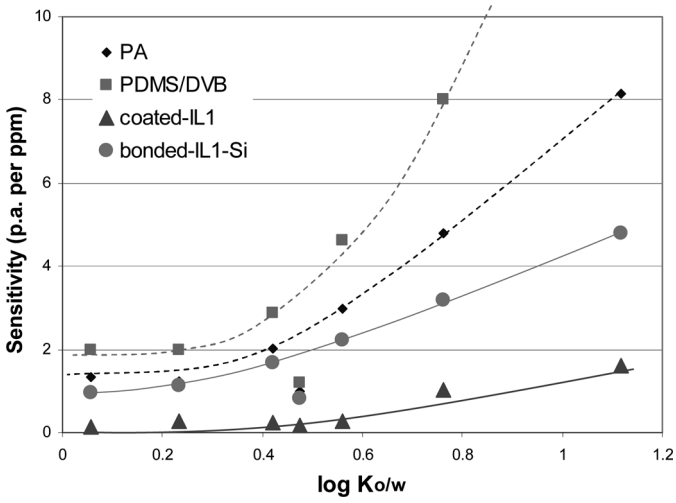

FIG. 5. Fiber response (expressed as the ratio peak area over ppm or μg/L) plotted versus the solute hydrophobicity (expressed as octanol/water partition coefficient, values listed in Table 2).

TABLE 1
Analytical performance data of the SPME headspace method

Compound	Linear range (μg/mL)	Regression equation (peak area)	r^2	LOD bonded-IL1-Si (μg/mL)[a]	LOD PDMS/DVB (μg/mL)[b]
Acetone	0.1–100	$9.855x + 0.898$	0.9999	0.062	0.071
Acetonitrile	0.1–100	$6.131x + 2.019$	0.9998	0.060	0.009
Butanol	0.1–100	$49.9x - 0.923$	0.9998	0.047	0.005
Ethanol	0.1–100	$12.82x + 1.82$	0.9991	0.084	0.41
Ethyl Acetate	0.1–120	$24.27x + 13.96$	0.9998	0.054	0.0017
Isopropyl alcohol	0.1–100	$11.79x - 6.566$	0.9982	0.069	0.048
Propanol	0.1–110	$20.156x - 3.62$	0.9998	0.086	0.074

[a]Determined with bonded-IL1-Si fiber.
[b]Determined with commercial PDMS/DVB 100 μm coated fiber.

Analytical Performances

The bonded-IL1-Si SPME fiber was tested for analytical capabilities. The headspace extraction procedure was evaluated by the determination of calibration curves (based on the peak area), detection limits, and precision for the analytes by using standard solutions. The results shown in Table 1 demonstrate that the linear range can reach 120 μg/mL. The limits of detection (LODs in μg/mL or ppm) were calculated according to the 3 s criterion (defined as three times the peak area standard deviation of the lowest concentration solution included in the calibration set and divided by the slope of the calibration curve) using a series of 6 solutions containing a low concentration and averaging, for each solution, the results of three coherent measurements. The values of LOD obtained with the bonded-IL1-Si fiber could be ten times higher than those obtained using the PDMS/DVB fiber (acetonitrile, butanol, ethyl acetate). For acetone, isopropyl alcohol, and propanol, the LODs were very similar with the two fibers (Table 1). The bonded-IL1-Si fiber was five times more sensitive for ethanol (LOD of 54 ng/mL or ppb) than the commercial PDMS/DVB fiber (LOD of 0.41 μg/mL, Table 1). Considering again the difference in absorbent volumes between the two fibers, the ionic liquid based fiber is very promising in the headspace SPME extraction of short chain polar alcohols.

TABLE 2
Hydrophobicity (log $K_{o/w}$), recovery, trueness, and precision of the studied compounds (n = 6)

Compound	Log $K_{o/w}$	Added (μg/mL)	Recovery (%)	Precision (%)
Acetone	0.234	0.502	103.0	3.4
		10.68	99.2	2.4
		52.12	99.0	0.7
Acetonitrile	0.474	0.512	103.0	11.5
		10.88	97.4	2.2
		53.12	100.1	1.3
Butanol	1.12	0.518	102.5	1.9
		11.00	102.9	0.4
		53.72	99.7	2.6
Ethanol	0.056	0.502	102.4	6.0
		10.68	104.2	1.1
		52.12	101.0	3.9
Ethyl acetate	0.761	0.574	109.5	0.4
		12.20	104.7	2.5
		59.56	102.0	0.6
Iso-propyl-alcohol	0.420	0.503	99.1	10.9
		10.69	102.0	1.8
		52.19	98.2	0.8
Propanol	0.560	0.514	100.6	16.4
		10.92	101.2	2.0
		53.32	99.4	2.3

Recovery studies were done using water spiked with the analytes at three levels of concentration in the 0.5–59.6 μg/mL range (Table 2). Satisfactory values between 97.4 and 109.5% of the spiked drug were obtained at each level of concentration. This indicates that the method is accurate (0.1–9.5%). Finally, the precision (RSD) was in the 0.7–16.5% range.

CONCLUSION

Ionic liquids have a high polarity associated to a low volatility that make them possible candidates as extracting material in SPME fibers (9–15). The simple IL coating of a fiber is not able to put enough material for extraction. Chemically attaching ILs to silica particles and gluing the IL-bonded particles in a thick 40 μm layer onto a fiber allow to enhance significantly the amount of IL extracting material. The studied bonded-IL1-Si fiber showed reproducibility comparable with that of two commercially

available SPME fibers tested in identical conditions. A slightly higher sensitivity for low molecular weight polar compounds in water was obtained with the IL fiber. This later result is very promising for the SPME analysis of small polar compounds since the extracting mass of the IL fiber was significantly lower than those of the two commercial fibers tested. The good thermal stability of the IL fiber allowed for fast thermal desorption of the extracted analytes in the hot injection port of the GC apparatus. The detection limits obtained with the IL fiber were somewhat higher than those obtained using the commercial PDMS/DVB and PA fibers due to the difference in active extracting mass between the fibers. Good recoveries, trueness, and precision were also obtained with all fibers and spiked samples.

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