

Abstract

As microextraction methods become more widely used to extract a greater number of analytes, the use of extraction media that can be readily tuned is of great interest. The unique properties of ionic liquids (ILs) and polymeric ionic liquids (PILs) has been exploited in the development of solid-phase microextraction (SPME) and single drop microextraction (SDME) techniques.

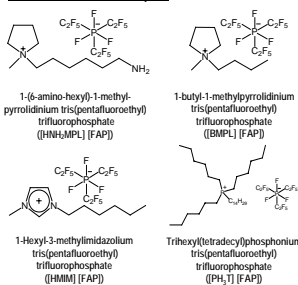
Tris(pentafluoroethyl)trifluorophosphate (FAP)-based ILs, known for their high hydrophobicity and hydrolytic stability, have been applied for the first time as extraction solvents for direct-immersion SDME studies coupled to high performance liquid chromatography (HPLC). Various functionalized FAP-based ILs employing phosphonium, imidazolium, and pyrrolidinium cations are compared and utilized as extraction solvents to selectively extract polycyclic aromatic hydrocarbons (PAHs) and small aromatic compounds from aqueous samples. The results demonstrated the proposed method, with high sensitivity and selectivity, is a versatile and efficient extraction method for the trace level determination of various kinds of target compounds.

The polymeric ionic liquid poly(1-vinyl-3-hexadecylimidazolium bis(trifluoromethyl)sulfonylimide) PIL was used as the extractant phase to direct extract mono- and polycyclic aromatic hydrocarbons from aqueous solutions by using SPME-GC method. The alkyl chain and the paired trifluoromethylsulfonyl imide counteranion impart the PIL highly hydrophobic properties which provided good reproducibility for the fiber in direct-immersion extractions. The results showed that by using the designed PIL for direct-immersion SPME, PAHs can be detected down to the part per trillion level.

Our group is also interested in utilizing task-specific ionic liquids (TSILs) as a novel class of sorbent coatings in SPME that are capable of selectively capturing and extracting CO₂. SPME coupled with gas chromatography (GC) was used to evaluate the performance of two different task-specific polymeric ionic liquids (PILs), namely poly(1-hexyl-3-vinylimidazolium) taurate [poly(HVIM-Taurate)], and poly(1-hexyl-3-vinylimidazolium) bis(trifluoromethyl)sulfonyl imide [poly(HVIM-NTf₂)] for the capture of CO₂. The extraction efficiency, calibration curves, and sample storage capacity of PIL coatings were evaluated and compared with commercial fibers. The results reveal that designed PIL coatings provide superior affinity and selectivity to CO₂.

Direct-Immersion Single Drop Microextraction

FAP-based Ionic Liquid



Advantages of FAP-based ILs in SDME

- Strong hydrophobic and hydrolytically stable nature make them great extraction solvents for direct-immersion SDME
- Can form stable and large volume of microdroplets
- Elute near the dead volume in reversed-phase HPLC
- Extraction selectivity can be easily controlled
- High solubility for different analytes

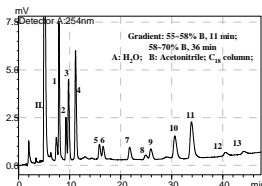
Comparison of the enrichment factor of 11 aromatic analytes with 4 studied FAP-based ILs by direct-immersion SDME

Analyte	ENRICHMENT FACTOR			
	[HMIM][FAP]	[HNH ₂ MPL][FAP]	[PH ₃ T][FAP]	[BMPL][FAP]
Nitrobenzene	101	33	113	76
α, α, α, 6-Tetrafluoro-m-holuidine	127	56	89	104
3-Tert-butylphenol	53	14	48	52
Ethyl benzoate	224	84	246	197
2-Nitronaphthalene	355	223	389	366
Naphthalene	387	301	486	442
Biphenyl	518	472	615	587
Acenaphthene	671	536	685	685
Fluorene	489	455	584	551
Phenanthrene	1881	1821	2145	2094
Anthracene	843	822	980	946

Selectivity control

The highest enrichment factors were obtained with the [PH₃T][FAP] IL for compounds with high molecular weight and fused rings while high enrichment factors were obtained for smaller, more polar molecules using the [HMIM][FAP] IL.

Conditions: Microdroplet volume, 6 μL; sample volume, 20 mL; extraction time, 120 min; stir rate, 400 rpm



➤ **Detection limit for 9 PAHs:**
Ranged from 0.1 to 0.6, 0.03 to 0.4, 0.04 to 0.7 and 0.1 to 1.2 μg L⁻¹ for [HMIM][FAP], [PH₃T][FAP], [BMPL][FAP] and [HNH₂MPL][FAP]

➤ **Reproducibility:**
RSD-1.5%-9.4%

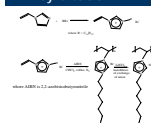
➤ **Recovery from real water samples:**
Tap water, 77-109%.
Creek water, 79-113%.
River water, 79-114%

Polymeric Ionic Liquid-Based Solid Phase Microextraction Coating for Direct-Immersion Extraction of Aromatic Compounds

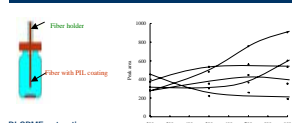
Summary

A polymeric ionic liquid (PIL) was used as the sorbent coating to perform direct-immersion SPME of mono- and polycyclic aromatic hydrocarbons from aqueous solutions. A linearity of three to four orders of magnitude was obtained with correlation coefficients better than 0.990. Compared with the commercial PDMS fiber of similar film thickness, the PIL coating provided much higher extraction efficiency, higher sensitivity, wider linear range and lower detection limits.

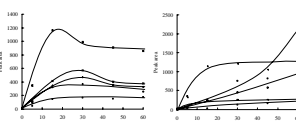
Synthesis of PIL



Optimization of DI-SPME Conditions



Dependence of extraction peak area on stir rate by using poly(VHIM-NTf₂) PIL fiber at room temperature. The extraction time was 30 minutes. The analytes shown in the graph are: 4000 μg L⁻¹ of benzene (●), toluene (○), nitrobenzene (▲), 1000 μg L⁻¹ of ethyl benzoate (□), and o-xylene (◇). 100 μg L⁻¹ of naphthalene (■), biphenyl (●), acenaphthene (▲), and phenanthrene (▲); 50 μg L⁻¹ of anthracene (▲).



The dependence of extraction peak area on the exposure times of the poly(VHIM-NTf₂) PIL fiber. The extractions were carried out with stir rate of 700 rpm. The studied analytes are: 4000 μg L⁻¹ of benzene (●), toluene (○), acenaphthene (▲), and nitrobenzene (▲), 1000 μg L⁻¹ of ethyl benzoate (□), and o-xylene (◇). 100 μg L⁻¹ of biphenyl (●), acenaphthene (▲), and phenanthrene (▲); 50 μg L⁻¹ of anthracene (▲).

Figures of merit of calibration curves using poly(VHIM-NTf₂) PIL

Analyte	Calibration range (μg L ⁻¹)	R	Slope ± SD (*10 ³)	Error of the estimate	LOD ^a (μg L ⁻¹)	%RSD ^b
benzene	320-12000	0.991	0.1 ± 5.6	65.7	nd ^c	11.3
toluene	3.2-18000	0.991	0.4 ± 17.2	306.8	2.80	10.7
ethyl benzoate	0.8-4000	0.993	1.4 ± 48.9	279.5	0.57	6.2
m, p-xylene	16-9000	0.991	1.7 ± 65.8	720.8	0.57	5.7
o-xylene	0.8-5000	0.994	1.6 ± 51.6	281.1	0.43	8.2
acenaphthene	20-30000	0.995	0.1 ± 3.3	131.0	12.29	12.9
nitrobenzene	20-30000	0.996	0.2 ± 5.2	212.3	12.84	12.9
nitrobenzene	3.2-32000	0.995	0.9 ± 21.7	940.6	1.22	14.2
naphthalene	0.08-800	0.999	5.8 ± 68.8	71.4	0.06	13.8
biphenyl	0.3-3000	0.992	13.1 ± 211.8	251.6	0.16	14.6
acenaphthene	0.3-900	0.996	15.9 ± 394.5	485.7	0.10	10.5
fluorene	0.08-900	0.993	15.1 ± 461.3	599.0	0.08	12.4
phenanthrene	0.08-900	0.995	17.0 ± 420.0	416.0	0.06	9.5
anthracene	0.15-450	0.990	7.3 ± 258.8	159.1	0.14	10.4

^a SD: error of the slope.

^b LOD: limit of detections calculated as three times of the signal to noise ratio.

^c Results obtained by three replicate extractions.

^d At lower concentrations the signal was overlapped with the background, therefore the LOD wasn't determined.

^e Conditions: 20 mL of sample volume; 30 minutes extraction; stir rate: 700 rpm.

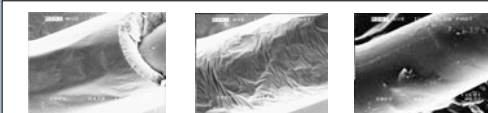
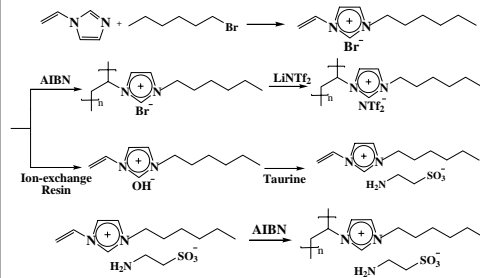
Recovery of the investigated analytes in water samples by poly(VHIM-NTf₂) PIL fiber^a

Analyte	Creek water		River water		Tap water	
	LC ^b	HC ^c	LC ^b	HC ^c	LC ^b	HC ^c
benzene	75.6 ± 1.0	84.9 ± 4.3	88.9 ± 10.5	82.8 ± 5.1	73.8 ± 0.9	80.0 ± 3.9
toluene	75.7 ± 9.9	109.6 ± 2.6	89.0 ± 15.4	107.5 ± 5.3	88.1 ± 14.9	81.5 ± 8.0
ethyl benzoate	90.8 ± 8.1	80.2 ± 1.4	114.3 ± 5.7	96.4 ± 2.1	116.6 ± 10.9	97.0 ± 12.3
m, p-xylene	82.0 ± 6.0	75.0 ± 2.9	99.2 ± 4.8	91.4 ± 3.1	98.9 ± 11.7	96.2 ± 14.2
o-xylene	82.0 ± 7.0	77.5 ± 1.6	91.2 ± 9.2	87.6 ± 1.2	100.2 ± 10.5	95.6 ± 11.8
acenaphthene	115.9 ± 4.4	115.9 ± 6.9	87.8 ± 3.2	78.9 ± 2.2	75.3 ± 8.2	112.0 ± 12.8
nitrobenzene	94.8 ± 13.0	115.1 ± 1.6	75.5 ± 10.7	78.1 ± 6.5	76.3 ± 13.6	92.8 ± 9.2
ethyl benzoate	110.2 ± 2.2	107.1 ± 9.1	71.9 ± 6.2	75.8 ± 14.4	111.5 ± 15.3	86.6 ± 10.9
naphthalene	103.3 ± 9.7	105.0 ± 5.2	74.8 ± 10.0	72.6 ± 7.9	111.7 ± 8.4	118.8 ± 12.8
biphenyl	98.1 ± 3.4	110.7 ± 10.1	88.2 ± 2.5	86.0 ± 14.7	107.4 ± 10.3	102.5 ± 11.9
acenaphthene	95.6 ± 4.0	100.4 ± 12.4	89.0 ± 7.3	75.6 ± 15.9	116.6 ± 9.8	111.7 ± 14.1
fluorene	95.2 ± 1.5	113.1 ± 15.9	86.5 ± 5.1	96.4 ± 15.4	113.9 ± 7.9	120.0 ± 10.8
phenanthrene	119.6 ± 13.3	117.2 ± 1.8	116.3 ± 12.1	107.7 ± 15.2	115.6 ± 9.9	120.2 ± 2.2
anthracene	87.4 ± 10.3	110.7 ± 15.8	81.3 ± 7.8	95.9 ± 1.6	107.5 ± 13.5	112.2 ± 12.5

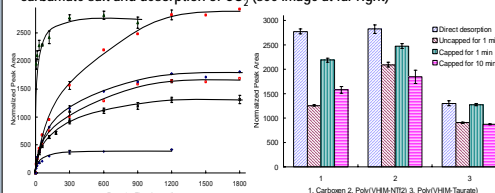
^a Relative recovery for n=3. ^b Low concentration level: 400 μg L⁻¹ of benzene, toluene, acenaphthene, nitrobenzene, and ethyl benzoate; 300 μg L⁻¹ of m, p-xylene; 150 μg L⁻¹ of ethyl benzoate, and o-xylene; 15 μg L⁻¹ of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 7.5 μg L⁻¹ of anthracene. ^c High concentration level: 4000 μg L⁻¹ of benzene, toluene, acenaphthene, nitrobenzene, and ethyl benzoate; 2000 μg L⁻¹ of m, p-xylene; 1000 μg L⁻¹ of ethyl benzoate, and o-xylene; 100 μg L⁻¹ of naphthalene, biphenyl, acenaphthene, fluorene, and phenanthrene; 50 μg L⁻¹ of anthracene.

Polymeric Task-Specific Ionic Liquids as Novel Stationary Phases in Solid-Phase Microextraction for Capture of CO₂

Two different types of polymeric task-specific ionic liquids were designed, synthesized and applied as novel SPME fiber coatings for the capture of CO₂. They were capable of capturing CO₂ via two different types of mechanism, namely physical sorption of poly(HVIM-NTf₂) PIL, and formation of complexation of poly(HVIM-Taurate)PIL due to the appended amino group that can react with CO₂ and form a carbamate salt. The synthetic approach is shown below:



SEM images were taken to show the surface morphology change for the poly(HVIM-Taurate) coating. It can be seen that smooth and even surface was obtained for the poly(HVIM-Taurate). After exposure of fiber to CO₂, a visible increase of viscosity and solidification was observed (see middle image above). The smooth surface can be regenerated by exposing the poly(HVIM-Taurate) coating to high temperature, resulting in decomposition of the carbamate salt and desorption of CO₂ (see image at far right)



Sorption time Profile (CO₂ pressure = 112 kPa) Examination of CO₂ Storage Capability

SPME fibers were coated with neat or binary PIL mixtures at desired compositions, and sorption profiles were obtained for these PIL-coated fibers as well as two commercial fibers, carboxen and PDMS. It was observed that the poly(HVIM-NTf₂) fiber (film thickness of approximately 10 μm) provided comparable extraction efficiency to the carboxen fiber (film thickness of 75 μm). The poly(HVIM-Taurate) fiber, on the other hand, appeared to possess superior storage capacity of CO₂. Calibration curves were obtained for the carboxen, the poly(HVIM-NTf₂), and the poly(HVIM-Taurate) fibers.

Figures of Merits of Calibration Curves

Fiber Coating Composition	Slope ± error	S _b ^b	Linear Range (kPa)	R ²
Carboxen (75 μm)	28.71 ± 1.67	119.3	1.5 - 75	0.980
Poly(HVIM-NTf ₂) (-10 μm)	23.28 ± 0.39	54.63	1.5 - 125	0.993
Poly(HVIM-Taurate) (-10 μm)	12.30 ± 0.35	49.62	1.5 - 125	0.992

Conclusion

The tunable properties of ionic liquids make them widely amendable for microextraction techniques. FAP-based ILs are significantly more hydrophobic and hydrolytically stable making them ideal candidates for the studies of direct-immersion SDME from large volumes of aqueous matrices. The selectivity and sensitivity of the extraction method can be tuned and manipulated by varying the cationic component of the IL, thereby providing larger enrichment factors for a variety of analytes, including polycyclic aromatic hydrocarbons (PAHs). PIL-base SPME demonstrated good reproducibility and high extraction efficiency and low detection limit for the extraction of PAHs when used in direct immersion extraction mode. Polymeric task-specific ionic liquids were proven to be able to capture CO₂ via different mechanisms, resulting in impressive extraction efficiencies, storage ability, sensitivity, as well as the capability to perform quantitative studies.

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