Use of Ionic Liquids for Liquid-Phase Microextraction of Polycyclic Aromatic Hydrocarbons

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This paper demonstrates, for the first time, that ionic liquids (IL) such as 1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$MIM][PF$_6$]) are excellent extraction solvents in liquid-phase microextraction (LPME). The unique properties of nonvolatility and adequate viscosity allow IL to be conveniently adopted as extraction solvents in both direct-immersion and headspace LPME. Model compounds, polycyclic aromatic hydrocarbons (PAHs), are conveniently and rapidly enriched in a 3-μL drop of [C$_8$MIM][PF$_6$] suspended on the tip of a microsyringe followed by liquid chromatographic determination. Compared to 1-octanol, a larger volume drop of [C$_8$MIM][PF$_6$] can be formed and survive for a longer extraction time; therefore, a much higher enrichment factor for PAHs can be reached. For low-volatility PAHs, direct-immersion LPME provides higher enrichment factors than that of headspace LPME. However, the enrichment factor obtained by headspace LPME was almost 3-fold of that by direct-immersion LPME in a 30-min extraction of the most volatile PAH, naphthalene. For 30-min direction-immersion LPME of EPA priority PAHs, the enrichment factor, correlation coefficient (R^2), and reproducibility (RSD, n = 5) were in the range of 42−166, 0.9169−0.9976, and 2.8−12%, respectively. Considering that IL can be easily prepared from relatively inexpensive materials and tuned by combination of different anions and cations for task-specific extraction of analytes from various solvent media, this proposed method should have great potentiality in sample preparation. Furthermore, the nonvolatility of IL makes it potentially useful for headspace LPME of volatile analytes.

Ionic liquids (IL) are ionic media resulting from combinations of organic cations and various anions. They may be liquids at room temperature. Their use as novel solvent systems for organic synthesis and catalysis has received a good deal of attention.[1] IL have several unique properties that make them useful in a variety of chemical processes. For example, they have no effective vapor pressure, the viscosity and the miscibility in water and other organic solvents can be tuned by changing the combination of different anions and cations of IL, and the preparation is easy from relatively inexpensive materials.[1,2] As a result of these properties, IL is emerging as an alternative recyclable medium for separation. Recently, IL were considered as attractive water-immiscible phases in liquid−liquid extraction.[3−5] IL were also used in organic solvent−supercritical CO$_2$ biphasic extractions[6−8] and in pervaporation.[4,9]

By using two typical IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$MIM][PF$_6$]) and the analogous chloride salt ([C$_4$-MIM]Cl), as stationary phases for gas chromatography, Armstrong et al.[10] studied the interactive and retentive behaviors of various compounds with IL. It was observed that the [C$_4$MIM]Cl interacted much more strongly with proton−donor and −acceptor molecules, while the [C$_4$MIM][PF$_6$] tended to interact more strongly with nonpolar solutes. More recently, Armstrong et al.[11] used a linear free energy approach to characterize IL and provided data that could be applied to help identify interactions and properties that are important for specific chemical applications.

Branco et al.[12] reported a novel method for highly selective separation of organic compounds by using a supported liquid membrane based on IL. Using [C$_4$MIM][PF$_6$] supported by a poly-(vinylidene fluoride) microporous membrane, diisopropylamine was selectively separated from a mixture of the organic isomeric

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amines hexylamine, diisopropylamine, and triethylamine in diethyl ether.

Furthermore, Visser et al.[13] prepared a series of task-specific IL for liquid−liquid extraction of Hg^{2+} and Cd^{2+} from water. By appending urea-, thiourea-, and thioether-substituted alkyl groups to imidazoles and combining the resulting cationic species with PF_6^-, IL phases are prepared into which Hg^{2+} and Cd^{2+} can be extracted with distribution ratios increased by several orders of magnitude. In a report by Huddleston et al.,[14] a series of hydrophilic and hydrophobic IL resulting from $[C_nMIM]$ ($n = 4$, 6, 8) cations and different anions were prepared and characterized to determine how water content, density, viscosity, surface tension, melting point, and thermal stability are affected by changes in alkyl chain length and anion. Abraham et al. correlated the partition coefficients (log P) between water and two IL with Abraham's solute descriptors to yield a linear free energy relationship. These can be used to predict further values of log P, to ascertain the solute properties that lead to increased or decreased log P, and to characterize the partition systems.[15]

More recently, Carda-Broch et al.[16] studied in detail the solvent properties of $[C_4MIM][PF_6]$ and determined the $[C_4MIM][PF_6]$/ water and $[C_4MIM][PF_6]$/heptane distribution coefficients for a set of 40 compounds, including organic acids, organic bases, amino acids, antioxidants, and neutral compounds.

The majority of the studies related to IL focus on their potential use in industrial processes, and limited efforts have been made to apply IL to analytical chemistry purposes. Shetty et al.[17] studied the applicability of alkylammonium nitrate and thiocyanate as a mobile phase in microcolumn reversed-phase liquid chromatography. Armstrong et al. adopted IL as stationary phases for gas chromatography[10,18] and as matrixes for matrix-assisted laser desorption/ionization mass spectrometry.[19] IL were also used as running electrolytes in aqueous[20] and nonaqueous[21,22] capillary electrophoresis, and an IL-coated capillary was prepared and investigated for DNA separation.[23] Chun et al.[24] reported the influence of structural variation in IL on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether.

Sample preparation is currently a bottleneck of analytical chemistry. Although most sample preparation can be accomplished by conventional procedures such as liquid−liquid extraction and solid-phase extraction (SPE), these methods suffer from the disadvantages of being time-consuming, using large amounts of toxic organic solvent, and being relatively expensive. Therefore, many efforts have been made to develop sample preparation methods that can overcome these disadvantages.

Recently, liquid-phase microextraction (LPME) has emerged as an attractive alternative for sample preparation. LPME can be performed by using a single drop of solvent[25−34] or a small length of porous hollow fiber-protected solvent.[35−37] LPME is commonly conducted in direct-immersion mode, but headspace extraction is also possible.[25,34,37] It has been demonstrated that LPME shows comparable extraction efficiency and reproducibility as the widely used solid-phase microextraction technique. The advantage of LPME is that it is inexpensive and there is considerable freedom in selecting appropriate solvents for extraction of different analytes.

The objective of this study is to exploit the potentiality of IL in sample preparation using the LPME technique. Considering that naphthalene[10] and fluoranthene[15] have relative large partition coefficients in the $[C_nMIM][PF_6]$/water ($n = 4$, 6) systems, IL drop-based direct-immersion and headspace LPME procedures were tried for extraction of polycyclic aromatic hydrocarbons (PAHs) from aqueous samples.

EXPERIMENTAL SECTION

Reagents. A mixed-PAH standard containing the Environmental Protection Agency (EPA) priority 16 PAHs was purchased from AccuStandard Inc. (New Haven, CT).An individual standard of benzo[k]fluoranthene and a mixed standard of fluorene, phenanthrene, and fluoranthene were obtained from Institute for Reference Materials of SEPA (Beijing, China). 1-Methylimidazole (99%), 1-chlorobutane (99%), 1-chlorohexane (95%), 1-chloroctane (99%), and hexafluorophosphoric acid (60 wt % solution in water) were obtained from Acros Organics (Geel, Belgium). HPLC-grade methanol and acetonitrile were purchased from Scharlace Chemie SA (Barcelona, Spain). All other chemicals were of analytical grade (Beijing Chemicals Corp., Beijing, China), and ultrapure water (EASYpure LF) was used throughout.

IL Synthesis. The syntheses of 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM][PF_6]$, 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$), and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) were conducted as described elsewhere.[2,3,10,38] Briefly, $[C_4MIM]Cl$ was prepared by adding equal amounts (0.2 mol) of 1-methylimidazole and 1-chlorobutane to a round-bottomed flask fitted with a reflux condenser and reacting for 48 h at 70 °C. $[C_6MIM]Cl$ and $[C_8-MIM]Cl$ were prepared by microwave synthesis in the following way:[38] (i) mixing 2 mmol of 1-methylimidazole and 1-chlorohexane

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Table 1. Some Physicochemical Properties of the Studied IL and 1-Octanol

	[C$_4$MIM][PF$_6$] measd	[C$_4$MIM][PF$_6$] lit.	[C$_6$MIM][PF$_6$] measd	[C$_6$MIM][PF$_6$] lit.	[C$_8$MIM][PF$_6$] measd	[C$_8$MIM][PF$_6$] lit.	1-octanol
MW		284		312		340	130
mp (°C)		10,[a] −8 [b]					−16[f]
glass transition temp (°C)		−80,[a] −77[c]		−78,[a] −80[c]		−82,[a] −66,[c] −70[d]	
density (g/mL)	1.37	1.36,[a] 1.37[d]	1.30	1.29,[a] 1.29[d]	1.20	1.22,[a] 1.22[d]	0.83[f]
viscosity (25 °C, cP)	393	450,[a] 312,[b] ∼148[h]	560	586[a]	710	682[a]	9.0[f]
surface tension (mJ/m^2, 63 °C)		42.9[g], 48.8 (dyn/cm,25 °C)[a]		43.4 (dyn/cm, 25 °C)[a]		32.8[g], 36.5 (dyn/cm, 25 °C)[a]	∼24.5[g]
chloride (ppm)	107	<3[e]	136		102	<14[e], 1400 ± 100[e]	
water content (mg/kg, dried)	920	590,[a] 0.72 (mol/L)[d]	545	472,[a] 0.02 (mol/L)[d]	366	388[a], 0.02 (mol/L)[d]	
water content (equilibrated)		11700 mg/kg[a] 0.92 mol/L[d] 2.3 ± 0.2%[e]		8837 mg/kg[a] 0.68 mol/L[d]		6666 mg/kg[a] 0.46 mol/L[d] 1.3 ± 0.5%[e]	3.5%[e]
solubility in water (g/100 mL)		1.88[c] 2.0 ± 0.3 (w/w, %)[e]		0.75[c]		0.20[c] 0.7 ± 0.1 (w/w, %)[e]	0.03[f]
UV cutoff absorbance (nm)	343		343		342		
conductivity (S m^{-1})		0.14[b]					

[a] Reference 14. [b] Reference 16. [c] Reference 24. [d] Reference 39. [e] Reference 40. [f] Reference 41. [g] Reference 42. [h] Reference 43.

Table 2. UV and Fluorescence (FL) Detection Conditions for HPLC Determination of PAHs

no.	name	time (min)	UV (nm)	FL (nm) excitn	FL (nm) emissn
1	naphthalene	0	254	218	357
2	acenaphthylene		254		
3	acenaphthene	19.00	254	226	359
4	fluorene				
5	phenanthrene	23.20		250	350
6	anthracene	24.20		250	425
7	fluoranthene	25.85		234	440
8	pyrene				
9	benz[a]anthracene, chrysene	29.00		286	405
10	benzo[b]fluoranthene	32.21		250	420
11	benzo[k]fluoranthene				
12	benzo[a]pyrene	35.00		294	460
13	dibenz[a,h]anthracene, benzo[ghi]perylene	36.10		298	420
14	indenol[1,2,3-cd]pyrene	38.00		246	490

or 1-chloroctane in test tube, which is put in a household microwave oven; (ii) irradiating the mixture for 30 s at 240 W; (iii) mixing again outside the oven for 10 s and then heating at the same power level for an additional 15 s. Step iii was repeated until the formation of a clear single IL phase. The produced [C$_n$-MIM]Cl (n = 4, 6, 8) were washed with ether and dried under vacuum at 80 °C.

[C$_n$MIM][PF$_6$] (n = 4, 6, 8) were prepared by slowly adding hexafluorophosphoric acid (0.13 mol) to the corresponding chloride (0.1 mol) in 100 mL of water. After stirring for 12 h, the lower liquid portion was washed with water until the washings were no longer acidic. The IL were cleaned up with Al$_2$O$_3$ and dried under vacuum at 80 °C. Caution: Hexafluorophosphoric acid is corrosive and toxic and must be handled with care, and the hydrolytic instability of [C$_n$MIM][PF$_6$] should also be considered.

Physicochemical Property. The obtained three IL were all colorless viscous liquids with physicochemical properties shown in Table 1. The density was determined by taking 50 μL of IL into a weighted vial with a 100-μL HPLC microsyringe to quantify its weight. The water content was determined using Karl Fischer titration. The viscosity was measured by a viscosity meter. The chloride content was determined with a modified spectrophotometric method.[44] Our experiment demonstrated that IL interfered with the spectrophotometric determination of chloride; thus, a standard addition procedure was adopted. The UV cutoff absorbance was determined by HPLC with an SPD-M10Avp diode array detector (Shimadzu).

It is clear from Table 1 that the three IL synthesized were not pure, and it should be noted that impurities such as the presence of chloride and nonequilibrated water would influence the physicochemical properties of the IL, as well as the partitioning and enrichment of PAHs.[43] Since the purpose of our study is to use IL for enrichment of PAHs (a set of stable analytes) for analytical purposes, the influence of the IL impurities on enrichment should be the same for samples and standards and could thus be eliminated. Therefore, no efforts were made to further purify our synthesized IL.

Instrument. The HPLC equipment used was an Agilent 1100LC including a BinPump, a VWD detector, and a FLD detector. For all compounds of interest, the VWD detector was set at 254-nm wavelength, and the excitation and the emission wavelength of the fluorescence detector was set as shown in Table 2. A personal computer equipped with an Agilent ChemStation program for LC systems was used to process chromatographic data. An Agilent Zorbax Eclipse XDB-C$_{18}$ column (150 × 4.6 mm, particle size 5 μm) was used as the analytical column.

Extraction Procdure. For the direct-immersion LPME procedure, 3 μL of IL was aspirated into a 50-μL microsyringe (Agilent), which was clamped so that the needle of the syringe was immersed into the 15-mL sample solution held in a vial. Then

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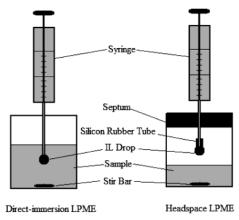(44) Florence, T. M.; Farrar, Y. J. *Anal. Chim. Acta* **1971**, *54*, 373−377.

Figure 1. Schematic diagram of the two different versions of liquid-phase microextraction (LPME).

Figure 2. Effect of various solvents on the peak area of PAHs: (a) 5 μg/L PAHs extracted for 5 min using 1 μL of solvent; (b) 1 μg/L PAHs extracted for 30 min using 3 μL of IL. Fl, fluorene; Phe, phenanthrene; Fluo, fluoranthene; B[k]f, benzo[k]fluoranthene.

the plunger was depressed to expose a 3-μL IL drop to the sample solution and the magnetic stirrer turned on. After stirring for the prescribed time, the IL drop was retracted into the microsyringe and injected into the HPLC system for analysis.

For the headspace LPME procedure, 10 mL of sample solution was placed in a 15-mL vial with septum. After the aspiration of 3 μL of IL, the needle of the microsyringe was used to pierce the vial septum, and the microsyringe was clamped into place so that the needle of the syringe was located in a consistent position of the headspace. Then the extraction was conducted as described above for immersed LPME. To suspend a 3-μL IL drop, the tip of the microsyringe needle was sheathed with a 3-mm-long silicon rubber tube (0.2-mm i.d and 2.8-mm o.d) as shown in Figure 1.
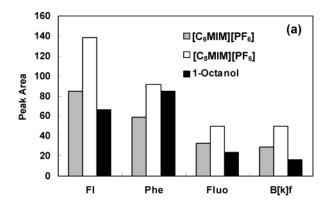
HPLC Separation. HPLC separation of PAHs was conducted by using a mixture of acetonitrile and water as mobile phase at a flow rate of 0.8 mL/min. The gradient profile was as follows: 40% acetonitrile for 0−5 min, increase to 85% acetonitrile during 5−25 min, and then to 100% acetonitrile during 25−40 min. Under these conditions, 12 PAHs were baseline separated. Benz[a]anthracene and chrysene, as well as dibenz[a,h]anthracene and benzo[ghi]-perylene, were coeluted because of the relatively short analytical column,. Therefore, the 12 PAHs shown in Table 1 were investigated in the following study.

RESULTS AND DISCUSSION

Two modes of LPME, direct-immersion LPME and headspace LPME, were investigated. Some parameters of the direct-immersion LPME such as type of IL, solvent drop volume, and extraction time were optimized using a mixed standard containing 1 μg/L (excepting specified) each of fluorene, phenanthrene, fluoranthene, and benzo[k]fluoranthene as model compounds. Then, the direct-immersion LPME was evaluated on the basis of enrichment factor, reproducibility, and linearity for the EPA priority PAHs.

Selection of IL. The alkyl part of the 1-alkyl-3-methylimidazolium hexafluorophosphate has significant influence on its physical and chemical properties, such as density, viscosity, and solubility,[14] that might affect the extraction efficiency of target analytes. Therefore, in this study, three IL including [C₄MIM]-[PF₆], [C₆MIM][PF₆], [C₈MIM][PF₆], and 1-octanol were compared as extraction solvents.

The experiments demonstrated that the largest drop volume that could be stably suspended on the needle tip of microsyringe
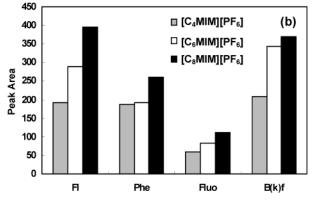
was 3 μL for IL and 1 μL for 1-octanol. Therefore, a drop volume of 1 μL was adopted for comparing the enrichment efficiency of 5 μg/L PAHs by using IL and 1-octanol as extraction solvent with an extraction time of 5 min. The results shown in Figure 2a indicate that [C₈MIM][PF₆] provided the largest peak area for all the studied PAHs. The result of [C₄MIM][PF₆] was not shown as a 1-μL droplet of [C₄MIM][PF₆] dissolved completely into the sample solution in 5-min extraction. Therefore, a 3-μL droplet was used for further comparing the enrichment of 1 μg/L PAHs by using the three IL as extraction solvent, and the results are shown in Figure 2b. Although Figure 2b shows that the largest analytical signals (peak area) were obtained when [C₈MIM][PF₆] was employed, it does not mean that the partition coefficients of PAHs in the [C₈MIM][PF₆]/water system are larger than the other systems. This is because LPME is a nonequilibrium procedure, and the obtained peak area is a complex result of various parameters including partition coefficient, the diffusion coefficient of the solute, the solubility of the extraction solvent in the sample solution, and the viscosity of both sample solution and solvent. Abraham et al.[15] calculated the partition coefficients (log P) of fluoranthene to be 4.22 and 3.75 for the [C₄MIM][PF₆]/water and [C₆MIM][PF₆]/water system, respectively. However, the results shown in Figure 2b indicate that the obtained peak area varied in the sequence [C₄MIM][PF₆] < [C₆MIM][PF₆] < [C₈MIM][PF₆]. The major reason is that the solubility of these IL varies in the same sequence (Table 1). It was observed in our experiments that, after 30 min of extraction, the volume of the survived IL droplet varied in the sequence [C₄MIM][PF₆] < [C₆MIM][PF₆] < [C₈MIM][PF₆]. From an analytical chemistry point of view, a
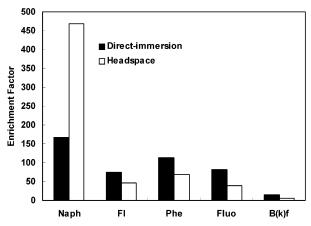
Figure 3. Comparison of enrichment factor between the direct-immersion and the headspace LPME of PAHs. Sample: 10 mL of 5 μg/L spiked PAHs in aqueous solution. Extractant: 3 μL of [C$_8$MIM]-[PF$_6$] drop. Extraction time: 30 min. Naph, naphthalene; Fl, fluorene; Phe, phenanthrene; Fluo, fluoranthene; B[k]f, benzo[k]fluoranthene.

Figure 4. Influence of extraction time volume on the peak area of PAHs. Sample: 20 mL 1 μg/L spiked PAHs in aqueous solution. Extractant: 3-μL [C$_8$MIM][PF$_6$] drop. ◆, fluorene; ■, phenanthrene; ▲, fluoranthene; ×, benzo[k]fluoranthene.

Figure 5. Effect of drop volume on the peak area of PAHs. Sample: 20 mL 1 μg/L spiked PAHs in aqueous solution. Extraction time: 30 min. ◆, fluorene; ■, phenanthrene; ▲, fluoranthene; ×, benzo[k]fluoranthene.

larger peak area is desirable to get a lower detection limit. Thus, [C$_8$MIM][PF$_6$] was selected as extraction solvent in the following studies.

Extraction Mode. LPME can be conducted in two modes, direct-immersion and the headspace extraction. One unique property of IL is that they have no effective vapor pressure even at high temperature. Therefore, it is reasonable to employ IL as extraction solvent for headspace LPME as the IL droplet exposed to the headspace can survive for a long time, permitting long-term extractions. The applicability of [C$_8$MIM][PF$_6$] for headspace LPME was evaluated by using naphthalene, fluorene, phenanthrene, fluoranthene, and benzo[k]fluoranthene as model compounds. Figure 3 compares the enrichment factor of the two extraction modes when samples spiked with 5 μg/L PAHs were extracted with 3 μL of [C$_8$MIM][PF$_6$] during extraction time of 30 min at room temperature (20 °C). As can be seen, for the low-volatility PAHs, the enrichment factor of headspace LPME was significantly lower than that of direct-immersion mode and the difference increased with increasing PAH molecular weight as expected. For the extraction of naphthalene, however, the enrichment factor by headspace LPME was almost 3-fold that of direct-immersion LPME. There are two reasons that might explain the much higher enrichment factor of headspace LPME of naphthalene. At first, there is no loss of [C$_8$MIM][PF$_6$] in headspace LPME during extraction as IL dose not evaporate. In direct-immersion LPME, some of the [C$_8$MIM][PF$_6$] is lost as it dissolves slightly in aqueous sample solution. The second reason is that headspace LPME shows a larger extraction rate as the extract needs not be transported through a liquid−liquid interface, which is the rate-determining factor in the direct-immersion procedure.

Considering that it could provide a higher enrichment factor for most PAHs, the direct-immersion LPME mode was adopted in the following study. However, it should be emphasized that the use of IL for headspace LPME of volatile compounds is a potentially useful application area demanding further investigation.

Extraction Time. Experiments showed that when a 3-μL droplet of [C$_8$MIM][PF$_6$] was suspended on the needle of a microsyringe and immersed in a 20-mL sample solution for extraction, the longest possible extraction time was 60 min. With
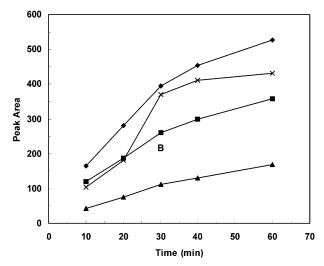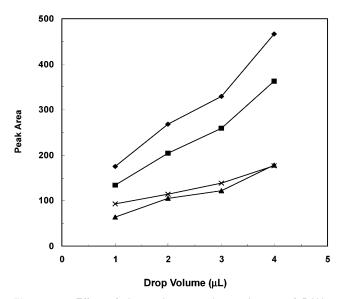
longer extraction times, the peak area decreased significantly and the reproducibility was lost, as most of the IL was dissolved in the sample solution. Figure 4 shows the influence of extraction time on the peak area of PAHs when a 3-μL droplet of [C$_8$MIM]-[PF$_6$] was used as extractant. As can be seen, the peak area increased with enrichment time over the whole range of 10−60 min.

In the following study, the enrichment time was set to 30 min. But according to Figure 4, an extraction time up to 60 min could be adopted if a larger enrichment factor is desired.

Drop Volume. The effect of [C$_8$MIM][PF$_6$] drop volume on the HPLC peak area was studied by exposing a drop to aqueous sample solution for 30 min. Results shown in Figure 5 indicate that the peak area increased with the drop volume over the range of 1−4 μL. Since the proposed LPME is a nonequilibrium procedure, the enrichment is a diffusion-controlled interfacial
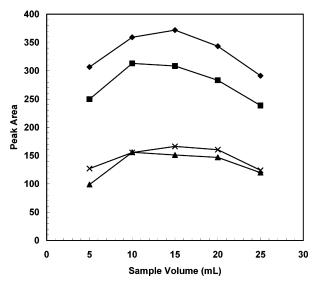
Figure 6. Effect of sample volume on the peak area of PAHs. Sample: 1 μg/L spiked PAHs in aqueous solution. Extractant: 3 μL of [C₈MIM][PF₆] drop. Extraction time: 30 min. ◆, fluorene; ■, phenanthrene; ▲, fluoranthene; ×, benzo[*k*]fluoranthene.

phenomenon. Therefore, as the drop surface increases with the drop volume, this results in a larger peak area. Figure 5 also shows that the lower the molecular weight of PAHs the more significant the increase in peak area. This probably is due to the diffusion rate of the PAH molecules, which decrease with molecular weight. Although a 4-μL drop gave larger peak area, it was occasionally dislodged by the stirred aqueous sample solution. A drop of 3 μL of [C₈MIM][PF₆] was adopted in the following study as it could stably persist on the needle of the syringe.

Sample Volume. Figure 6 shows the relationship between the peak area and the sample volume, which indicates that for the four studied PAHs the largest analytical response was obtained when 10−15 mL of sample was extracted. A larger sample volume gave a smaller peak area because more [C₈MIM][PF₆] was dissolved into the sample solution, leaving less residual IL to be injected into the HPLC system for detection.

Addition of Organic Solvent. Due to the low aqueous solubility of PAHs, an organic solvent such as methanol, acetonitrile, or 2-propanol is usually added to the sample solution to prevent their adsorption onto the vessel surface and thus to increase the recovery in SPE.[45] In this work, the effect of 2-propanol on peak area was studied by extracting PAH solutions with different concentrations of 2-propanol. Results shown in Figure 7 demonstrated that the 2-propanol concentration was a critical parameter. The peak of the relatively high molecular weight benzo[*k*]fluoranthene increased with 2-propanol concentration, probably because the addition of 2-propanol significantly decreased the viscosity of the sample solution and thus increased the diffusion rate of benzo[*k*]fluoranthene. Another possible reason is that the addition of 2-propanol decreased the adsorption of benzo[*k*]fluorantheneonto on the vessel surface. However, the increase of 2-propanol concentration increased the dissolved amount of the [C₈MIM][PF₆] drop in the sample solution, leading to low analytical response for the low molecular weight PAHs such as fluorene, phenanthrene, and fluoranthene. This was because
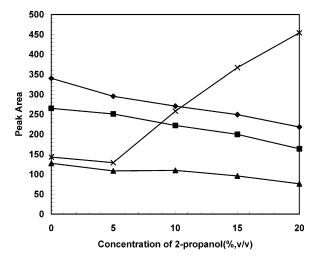
(45) Marce, R. M.; Borrull, F. *J. Chromatogr., A* **2000**, *885*, 273−290.

Figure 7. Effect of 2-propanol concentration in aqueous sample on the peak area of PAHs. Sample: 15 mL of 1 μg/L spiked PAHs in aqueous solution. Extractant: 3 μL of [C₈MIM][PF₆] drop. Extraction time: 30 min. ◆, fluorene; ■, phenanthrene; ▲, fluoranthene; ×, benzo[*k*]fluoranthene.

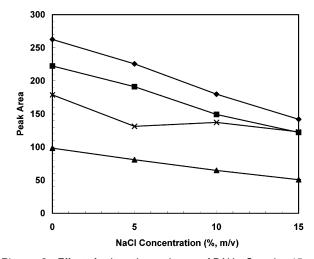**Figure 8.** Effect of salt on the peak area of PAHs. Sample: 15 mL of 1 μg/L spiked PAHs in aqueous solution. Extractant: 3 μL of [C₈MIM][PF₆] drop. Extraction time: 30 min. ◆, fluorene; ■, phenanthrene; ▲, fluoranthene; ×, benzo[*k*]fluoranthene.

the diffusion rate of low molecular weight PAHs was relatively larger and the adsorption onto the vessel surface was less significant. Thus, their peak areas were mainly dependent on the amount of [C₈MIM][PF₆] remaining in the drop that is injected for determination. A concentration of 15% (v/v) 2-propanol was adopted as a compromise in the following studies.

Salt Effect. In traditional liquid−liquid extraction, the addition of salt often increases the extraction efficiency due to the salting-out effect. Wang et al.[30] investigated the effect of salt on LPME, and it was reported that the extraction efficiency decreased with the increase in sodium chloride concentration. In this study, the salt effect on LPME of PAHs by IL was investigated by adding different amounts of sodium chloride to the sample and the results are shown in Figure 8. As can be seen, the peak area decreased with the increase of sodium chloride concentration in the studied range of 0−15% (w/v). Performing extraction in higher concentrations of sodium chloride was difficult as it was not easy to firmly suspend the IL drop. It was observed that the size of the residual

Table 3. Enrichment Factor, Linearity, and Reproducibility for Extraction of 12 PAHs by the Proposed Direct-Immersion LPME Method[a]

analyte	enrichment factor	corr coeff (R^2)	reproducibility (RSD, %, $n = 5$)
naphthalene	166	0.9169	9.9
acenaphthylene	95	0.9670	12
acenaphthene	90	0.9790	11
fluorene	97	0.9976	11
phenanthrene	131	0.9957	12
anthracene	105	0.9974	11
fluoranthene	106	0.9906	9.8
pyrene	109	0.9933	7.8
benzo[b]fluoranthene	61	0.9976	7.8
benzo[k]fluoranthene	47	0.9690	9.8
benzo[a]pyrene	66	0.9702	3.1
indenol[1,2,3-cd]pyrene	42	0.9846	2.8

[a] Conditions: extractant, 3 μL of [C$_8$Mim][PF$_6$]; sample, 15 mL of PAHs spiked in 15% (v/v) 2-propanol solution; extraction time, 30 min.

IL droplet after the selected time of extraction was unchanged when different concentrations of sodium chloride were added to the sample solutions. On the other hand, it was reported that the addition of salts in the aqueous phase did not increase the water content in the IL phase.[39] Thus, the decrease of peak area with the increase of sodium chloride concentration did not result from the dissolving of the IL drop in sample solution. The reason for the decrease of peak area is not clear. Probably it is because the diffusion rate of the PAH molecules, from the bulk sample solution to the IL drop, decreased with the increase of viscosity of bulk sample solution resulting from the increasing of sodium chloride concentration.

Method Evaluation. To evaluate the proposed IL-based direct-immersion LPME method, some parameters such as linearity, reproducibility, and enrichment factor for the EPA priority PAHs were determined under the above optimized conditions. Linearity was investigated over a concentration range of 0.5−5 μg/L for benzo[k]fluoranthene, benzo[a]pyrene, and indenol[1,2,3-cd]-pyrene and 0.5−10 μg/L for the other PAHs. The reproducibility was determined by five repeated extraction of a 5 μg/L spiked water sample. Results shown in Table 3 indicate that, for all the studied PAHs, good linearity with correlation coefficients ranging from 0.9169 to 0.9976 was obtained. The relative standard deviations (RSD, $n = 5$) were between 2.8 and 12%. The enrichment factors, which decreased with the PAHs' molecular weights due to decrease of the molecule diffusion rate, were in the range of 42−166 with an enrichment time of 30 min. According to Figure 4, it is obvious that a larger enrichment factor can be obtained if the enrichment time increased to 60 min.

CONCLUSION

This study demonstrated that the IL [C$_8$MIM][PF$_6$] is an excellent extractant for LPME of PAHs. The unique property of nonvolatility and adequate viscosity allows this IL to be conveniently adopted as extractant in direct-immersion and headspace LPME. Compared to 1-octanol, [C$_8$MIM][PF$_6$] provides higher extraction efficiency, longer possible extraction time, and much larger drop volume, and thus higher enrichment factor. While a larger enrichment factor was obtained by direct-immersion LPME for most of the studied compounds, the enrichment factor obtained by headspace LPME of naphthalene is almost 3-fold that by direct-immersion LPME, which indicates that headspace LPME is superior to direct-immersion LPME when volatile analytes are extracted.

Although IL are relatively expensive, the proposed IL-based LPME procedure is an inexpensive and one-step microextraction technique as only 3 μL of IL was used for each determination. Since IL can be easily synthesized in the laboratory from relatively inexpensive materials and tuned by combination of different anions and cations for task-specific extraction of analytes in various solvent mediums, the method proposed in this paper will have a broad potential in sample preparation, although much more detailed studies regarding both the theoretical and practical aspects should be conducted. It should especially be emphasized that the nonvolatile property of IL makes it potentially useful for headspace LPME of volatile compounds, and this warrants further investigation.