Ionic liquid-containing semipermeable membrane devices for monitoring the polycyclic aromatic hydrocarbons in water

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Abstract

Ionic liquid-containing semipermeable membrane devices (IL-SPMDs) were developed to monitor the polycyclic aromatic hydrocarbons in water. Uptake kinetics of naphthalene, 1-methylnaphthalene, phenanthrene, pyrene, chrysene by layflat low-density polyethylene tubing (15 cm × 2 cm) filled with 0.5 ml 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid were studied in a laboratory continuous-flow system for the duration of 16 days. The device concentration factors were in the range of 830–7800 for the studied PAHs. The kinetic parameters of IL/water partition coefficients, analytes uptake rate constants and sampling rates were estimated using mathematical models. These parameters were used in the field experiment to estimate the concentrations of the PAHs in Lanzhou section of Yellow River in China, with the result in comparison with that obtained by triolein-SPMD.
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1. Introduction

In-situ monitoring of organic compounds with biological surrogates is a technology receiving an increasing attention. Several designs of membrane samplers have been proposed, and all of them are based on the theory that lipophilic compounds will passively diffuse from the water column into a lipophilic phase. Södergren (1987) and Hasset et al. (1989) have respectively reported passive monitors based on hexane contained by regenerated cellulose dialysis tubing and polyethylene membranes for sequestering contaminants from aqueous environments, as well as cellulose dialysis membranes contain-

ing micellar receiving solvent (Pekol and Cox, 1995) and polyethylene tubes filled with isooctane (Peterson et al., 1995). Huckins et al. (1990) developed lipid-containing semipermeable membrane devices (SPMDs) which have recently become favoured as an effective option for passive preconcentration of organic contaminants in environment.

Although lipid-containing SPMDs have been successfully used in a variety of field studies (Rantalainen et al., 1998, 2000; Johnson et al., 1995; Lohmann et al., 2001; Kelly et al., 2002), the method suffers from the disadvantages of adopting toxic organic solvent for dialysis, and following clean-up and concentration steps. To incorporate the principles of Green Chemistry, new methods should be developed to overcome these disadvantages.

Ionic liquids (ILs) have aroused interest for their promising role as alternative green solvents. They are

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ionic media that result from combination of organic cations and various anions and exist as liquid at room temperature. ILs have several unique properties that make them useful in a variety of chemical processes (Blanchard and Brennecke, 2001; Renner, 2001; Richard et al., 2002). For example, they are nonvolatile, nonflammable, and good solvents for a wide range of both organic and inorganic compounds. Recently, ILs were considered as attractive water-immiscible phase in liquid–liquid extraction (Wei et al., 2003). Visser et al. (2002) prepared a series of task-specific IL for extraction of Hg^{2+} and Cd^{2+} from water. Furthermore, IL-based liquid-phase microextraction was developed as sample preconcentration procedure for organic contaminant (Liu et al., 2003, 2004).

To exploit the potentiality of IL for replacing traditional solvents, in this study, we applied ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) in semipermeable membrane (IL-SPMD) as a sampler to monitor polycyclic aromatic hydrocarbons in water. The analytes in the ionic liquid were directly analyzed by HPLC without the step of organic solvent-consuming dialysis. The laboratory study was conducted to obtained the uptake curve and calculate kinetic parameters. These parameters were used in a preliminary field study to estimate the PAH concentrations in comparison with those estimated by the method of triolein-SPMD.

2. Materials and methods

2.1. Materials

Standard PAHs naphthalene, phenanthrene, pyrene and chrysene were obtained from Acros Organics. 1-methylnaphthalene was purchased from Tokyo Kasei Kogyo, Japan. Semipermeable membrane (low-density polyethylene (LDPE) tubing, 2.5 cm in width, 75 μm in thickness) was obtained from Environmental Sampling Technologies (EST) lab (St Joseph, MO, USA). Reagents for synthesis of IL including 1-methylimidazole (99%), 1-chlorobutane (99%) and hexafluoro- phosphoric acid (60 wt.% solution in water) were obtained from Acros Organics. HPLC-grade methanol and acetonitrile were purchased from Scharlace (Barcelona, Spain). All the other chemicals were analytical grade reagents from Beijing Chemicals Co. (Beijing, China).

2.2. IL Synthesis

1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) was synthesized as described elsewhere (Huddleston et al., 1998). Briefly, $[C_4MIM]Cl$ was prepared by adding equal amount (0.3 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 until a yellow viscous liquid is formatted. The viscous liquid was then cooled and washed with ethyl acetate and dried under vacuum at 80 °C to remove the solvent. $[C_4MIM][PF_6]$ was prepared by slowly adding hexafluorophosphoric acid (0.13 mol) into $[C_4MIM]Cl$ (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 was cleaned up with Al_2O_3 and dried under vacuum at 80 °C.

2.3. Preparation of SPMDs

Semipermeable membrane devices were prepared in a way similar to that described by Huckins et al. (1990). Layflat low-density polyethylene (LDPE) tubing, soaked beforehand in hexane to remove contaminants, was cut into 18 cm long segments. We pipetted 0.5 ml ionic liquid $[C_4MIM][PF_6]$ into each segment of LDPE tubing, spreading the ionic liquid into thin films, and then heat-sealed the tubing at each end. The effective length of IL-SPMD was 15 cm.

2.4. Laboratory flow-through exposures

A set of 28 IL-SPMDs was placed in an exposure chamber (20 L in volume) which was connected to a continuous-flow system. A concentrated mixture of the five PAHs in water contained in a stock bottle was added into the main water flow to the chamber by a peristaltic pump. The overall flow rate through the exposure chamber was maintained at 42 $ml\,min^{-1}$ to obtain relatively stable concentrations of the different PAHls in the exposure chamber (Table 1). In the exposure chamber, the IL-SPMDs were suspended vertically from stainless steel rings whose centrums were the input points of exposure water. The PAH stock bottle was amber glass and light was maintained at the minimal level to reduce the potential for photolysis. The experiment lasted for 384 h. During the experiment, duplicate SPMDs tubes from the exposure chamber were sampled for each time point of 2, 4, 6, 8, 13, 24, 48, 72, 96, 144, 192, 240, 312, and 384 h. In experimental duration, triplicate sample of water were taken every second day to monitor the concentrations of the PAHs in the exposure chamber.

Ten microliters of IL were aspirated into a 50μl microsyringe and injected into the HPLC for separation and quantification of the PAHs. The properties and concentrations of the studied PAHs in the exposure chamber were shown in Table 1. The experimental temperature was 19 °C.

2.5. Field study

Field exposure of the IL-SPMDs was studied in Lanzhou section of Yellow River in China and compared with that of triolein-SPMDs. In this study, four

Table 1
Properties of the studied PAHs and concentrations in exposure chamber

Compound	MW	Water solubility (mg/l)[a]	Conc. in the exposure chamber, $\mu g l^{-1}$ (Mean $\pm$ SD), $n = 8$
Naphthalene	128	30.2	0.136 ± 0.021
1-Methylnaphthalene	142	28.5	0.075 ± 0.011
Phenanthrene	178.2	1.20	0.034 ± 0.009
Pyrene	202.3	0.135	0.292 ± 0.052
Chrysene	228.3	0.0028	0.270 ± 0.048

[a] Data cited from literature.

sampling sites along the river were selected. They were: site 1 near the Guandao Bridge affected by the industrial water of Lanzhou oil refinery; site 2 at the outfall of the effluent sewerage from the industrial park; site 3 at Bapan Canyon, upper reaches of the Lanzhou section of Yellow River; and site 4 at the Zhongshan Bridge affected by the domestic sewage.

Semipermeable membranes of 30 cm in length filled with 1 ml IL (the same ratio of membrane surface-to-volume of IL as the laboratory experiment) were prepared for deployment at the field site. At the same time, standard triolein-SPMDs (1 ml triolein in semipermeable membranes of 91.4 cm in length) were prepared in the similar way as described by Huckins et al. (1990). The SPMDs were placed into an airtight glass container and transported to Yellow River in Lanzhou city. Two IL-SPMDs and two triolein-SPMDs were placed in a stainless steel cages deployed at each site. The cages were suspended 1 m below the surface. After five days of exposure, the SPMDs were taken to the laboratory (each in a separate glass vial) where they were rinsed with tap water and dried by absorbent cotton. Ten microliters of IL were aspirated from the IL-SPMDs and injected into the HPLC to analyze the concentrations of PAHs. The triolein-SPMDs were transferred into beakers containing 40 ml of cyclohexane, and dialysed for 24 h. The SPMDs were removed and the solvent were passed through anhydrous sodium sulfate and evaporated to dryness in a rotary evaporator. The residue was then redissolved with 2 ml of methanol and analyzed for the PAHs by HPLC.

2.6. Instrument analysis

The HPLC equipment was equipped with a water 1525 Binary Pump, an 2475 multi-fluorescence detector, and a personal computer (Millennium[32] workshop for chromatographic data processing). An SUNIEK Kromasil C18 column (200 mm × 4.6 mm, particle size of 5 μm) was used for separation of the enriched analytes. The mobile phase was a mixture of acetonitrile–water (80:20 (v/v)) at a flow rate of 1 ml min^{-1}. The wavelength of excitation and emission was set at $x\lambda$ 280 nm and $e\lambda$ 355 nm for zero minute, $x\lambda$ 250 nm and $e\lambda$ 420 nm for 9 min, and $x\lambda$ 280 nm and $e\lambda$ 355 nm for 12 min.

2.7. Mathematical models

To describe the overall uptake curve of the PAHs by the IL-SPMDs, we used kinetic equations proposed by Huckins et al. (1993) based on a one-compartment bioconcentration model:

$$C_I = C_W K_{I/W}(1 - \exp(-k_o K_{MW} A T / K_{I/W} V_I)) \quad (1)$$

Simplifying and solving for ambient water concentration:

$$C_W = C_I / K_{I/W}(1 - e^{-k_u t}) \quad (2)$$

In these equations, C_I is the concentration of analyte in IL contained in SPMD, C_W is analyte concentration in water, $K_{I/W}$ is the operational equilibrium IL/water partition coefficient, k_o is the overall mass-transfer coefficient, K_{MW} is the equilibrium membrane–water partition coefficient, A is the surface area of the IL-SPMD, V_I is the volumes of the ionic liquid, k_u is the overall uptake rate constant, and t is the time. In the triolein-SPMD method, the membrane is expressed as a lipid-equivalent volume of sampling medium, so C_I is defined on the basis of the total amount of analytes accumulated by the whole SPMD, i.e., triolein + polyethylene membrane. While in IL-SPMD method, from the practical point of view, the analytes in the IL were analyzed directly without regarding to the amount of analyte in the membrane.

Concentrations of the analytes in water (C_W) and in the ionic liquid (C_I) were two direct parameters measured regularly during the continuous-flow study. $K_{I/W}$ and k_u were estimated through fitting Eq. (2) to the kinetic data using the SPSS 12.0 software for windows and its Marquardt–Levenberg least-squares, with t being independent variable, C_I dependent variable, and C_W constant.

3. Results and discussion

3.1. Uptake of the PAHs in flow-through experiment

Uptake curve of the PAHs were shown in Fig. 1. Due to the rapid binding of the PAHs by the LDPE material, the PAH concentrations in the water chamber decreased
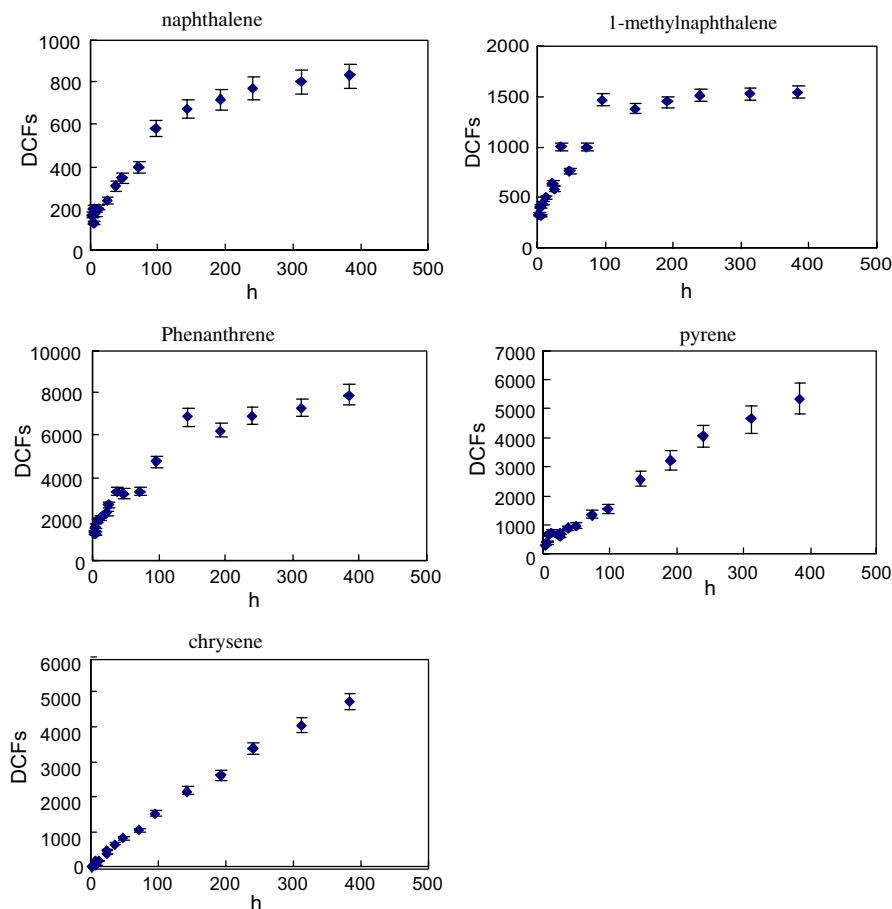
Fig. 1. IL-SPMD uptake profiles of five PAHs (DCFs, ratio of PAH concentration in ILs to that in water, C_I/C_W).

during the very beginning of the experiment and became stable after 2 h. Therefore, the data obtained before 2 h were excluded from kinetic analysis. During the exposure period of 16 days, naphthalene, 1-methylnaphthalene and phenanthrene were concentrated fast by IL-SPMD, experiencing linear and curve region of uptake and approaching the steady state, but for compounds pyrene and chrysene, the uptake remained in the linear uptake phase. The enrichment of SPMD was larger for more hydrophobic compounds phenanthrene, pyrene and chrysene with the device concentration factors (DCFs, ratio of PAH concentration in IL to that in water, or C_I/C_W) approached 5000–7800 during experiment period, but for less hydrophobic compounds of naphthalene and 1-methylnaphthalene the DCFs ranged from 830 to 1500.

3.2. Uptake kinetics

A good fit of kinetic equation (2) to the experimental data was obtained for all the studied PAHs. The r^2 values for the regression ranged from 0.88 to 0.99. Coeffi-

cient of variation for $K_{I/W}$ and k_u was less than 19 and 24%, respectively (Table 2).

3.3. Prediction of analyte concentrations in water

One way to predict analyte concentration in the water from their levels in SPMDs is using the values of $K_{I/W}$ and k_u fitting the Eq. (2). It is obvious that the accuracy of the estimated parameters in Eq. (2) increases as the system approaches equilibrium. Therefore it is most commonly used to estimate C_W toward the curvilinear phase of uptake process (i.e., $K_{I/W} > C_I/C_W > 0.693 \, K_{I/W}$). However, for the chemicals requiring a long time to reach the steady state, the C_W can be estimated from the data obtained from linear phase in order to fulfill the study objective.

When k_u is very small or $C_I/C_W \leqslant K_{I/W}$, chemical uptake is linear, the Eq. (1) can be reduced to

$$C_I = C_W k_o K_{MW} A T / V_I = C_W R_S T / V_I \qquad (3)$$
$$R_S = k_o K_{MW} A = k_u K_{I/W} V_I \qquad (4)$$

Table 2
Estimated IL-SPMD uptake kinetic parameters of the test compounds

Compound	$K_{I/W}$		k_u (h^{-1})		r^2
	Estimate	CV[a], %	Estimate	CV[a], %	
Naphthalene	8.05×10^2	6.6	0.0129	18.5	0.9038
1-Methylnaphthalene	1.47×10^3	5.3	0.0246	17.0	0.8857
Phenanthrene	1.46×10^4	6.9	0.0138	19.5	0.8830
Pyrene	9.64×10^3	7.5	0.0017	9.6	0.9987
Chrysene	8.55×10^3	18.6	0.0025	23.6	0.9776

[a] CV, variation coefficient (%).

where V_I is the volume of the IL, R_S is the sampling rate of the IL-SPMD, representing the volume of water extracted per day, and t is the sampling time. With R_S estimated by Eq. (4), C_W can be estimated by Eq. (3) for the analytes in the linear uptake phase toward the end of the exposure period.

Usually, for the first-order uptake kinetics of a chemical, linear phase can be assumed for the initial halftime $t_{1/2}$ (the time required to reach 50% equilibrium concentration in the IL, $t_{1/2} = (0.693 K_{I/W} V_I)/R_S$). Based on the $K_{I/W}$ and k_u values, we calculated the $t_{1/2}$ values and R_S values (0.5 ml IL) of the studied PAHs (Table 3).

When $C_I/C_W \approx K_{I/W}$, C_W can be determined using an equilibrium equation:

$$C_W = C_I/K_{I/W} \qquad (5)$$

Usually when $t >$ four $t_{1/2}$ s, the concentrations of analytes in IL reach >90% of the equilibrium concentration in an IL-SPMD and the uptake approach the steady state.

Estimates of R_S indicated that phenanthrene was sampled at the highest rate, followed by 1-methylnaphthalene, pyrene and chrysene. Naphthalene was sampled at the lowest rate. The critical factors determining the rate of permeation in such a system are membrane surface area, the concentration gradient across the membrane, and the permeation coefficient (Södergren, 1987). Huckins et al. (1990) suggested that, for most chemicals, permeation through polyethylene membrane is the rate-limiting step of the SPMD sampling. In our experiment conditions, the difference of sampling rate was probably dependent on the hydrophobicity and

Table 3
IL-SPMD sampling rate (0.5 ml IL) and $t_{1/2}$ values of the test compounds

Compound	R_S (l day^{-1})	$t_{1/2}$ (day)
Naphthalene	0.125	2.23
1-Methylnaphthalene	0.436	1.17
Phenanthrene	2.419	2.09
Pyrene	0.202	16.50
Chrysene	0.261	11.37

molecular dimensions of analytes. The permeation would be faster with stronger hydrophobicity and smaller size of the PAH molecules, which can used to explain why phenanthrene (intermediate hydrophobicity and size) had the fastest sampling rate in comparison with the other PAHs. Another possible reason determining R_S is the solubility of PAHs in the [C$_4$MIM][PF$_6$], which probably be explained by the local electrostatic interaction of the IL and PAHs. Based on the definition of $t_{1/2}$, higher $K_{I/W}$ and lower R_S leaded to larger value of $t_{1/2}$, so pyrene and chrysene had longer halftime.

3.4. Field study

The primary purpose of SPMDs is to estimate average concentrations of pollutants in water. IL-SPMDs and triolein-SPMDs were deployed for 5 days at each site, and contaminant residues were measured. The water concentrations of PAHs studied were predicted for the triolein-SPMDs according to Huckins et al. (1993, 1999). 1-methylnaphthalene was excluded, because it's kinetic parameters could not be found. For IL-SPMDs method, in the sampling period, only 1-methylnaphthalene approached the steady state, while pyrene and chrysene remained linear uptake region; naphthalene and phenanthrene were in curve uptake region. So, average water concentrations of PAHs were estimated from Eq. (5) for 1-methylnaphthalene; and Eq. (3) for pyrene and chrysene; and Eq. (2) for naphthalene and phenanthrene based on above kinetic parameters.

Tables 4 and 5 showed the concentrations of target PAHs in the tow kinds of SPMDs and estimate concentration in water using two methods, respectively. For the concentrations of the PAHs in SPMD, the values for IL-SPMD (64.80–25986 μg l^{-1}) were several fold lower than those for triolein-SPMD (710–86720 μg l^{-1}). This is because the amounts of PAHs includes those both in the triolein and in polyethylene membrane for triolein-SPMDs, but only the amount in IL (not in polyethylene membrane) for IL-SPMDs. Another reason was due to the larger ratio of membrane surface-to-volume of the triolein-SPMD. Comparing with the estimated

Table 4
Analyte concentrations in the triolein-SPMDs and IL-SPMDs in the field study

Compound	Site 1 ($\mu g\,l^{-1}$)		Site 2 ($\mu g\,l^{-1}$)		Site 3 ($\mu g\,l^{-1}$)		Site 4 ($\mu g\,l^{-1}$)	
	IL-SPMD	Triolein-SPMD	IL-SPMD	Triolein-SPMD	IL-SPMD	Triolein-SPMD	IL-SPMD	Triolein-SPMD
Naphthalene	102.48	3320	1450.2	10590	16.46	7190	91.63	3340
1-Methylnaphthalene	185.12		2619.2		98.25		152.86	
Phenanthrene	286.74	1340	25986	48290	316.14	1090	467.67	1090
Pyrene	23.60	2390	2485.6	86720	23.56	1040	18.20	1130
Chrysene	38.95	1330	747.63	23180	64.80	710	15.26	990

Each value represents the mean for two-independent experiments performed in duplicate, with average standard deviation < 5%.

Table 5
Estimated water concentrations of PAHs from the field study using triolein-SPMDs and IL-SPMDs

Compound	Site 1 ($\mu g\,l^{-1}$)		Site 2 ($\mu g\,l^{-1}$)		Site 3 ($\mu g\,l^{-1}$)		Site 4 ($\mu g\,l^{-1}$)	
	IL-SPMD	Triolein-SPMD	IL-SPMD	Triolein-SPMD	IL-SPMD	Triolein-SPMD	IL-SPMD	Triolein-SPMD
Naphthalene	0.10	0.24	1.42	1.96	0.05	0.16	0.09	0.02
1-Methylnaphthalene	0.13		1.77		0.07		0.10	
Phenanthrene	0.02	0.05	1.44	1.24	0.02	0.06	0.03	0.05
Pyrene	0.01	0.03	1.24	1.78	0.01	0.04	0.01	0.04
Chrysene	0.02	0.04	0.28	0.80	0.03	0.03	0.01	0.03

Each value represents the mean for two-independent experiments performed in duplicate, with average standard deviation < 5%.

concentrations of PAHs in water (in Table 5), we can see, the DCF of the SPMDs came up to 10^3–10^5 after only 5 day's sampling. Though the DCF of IL-SPMDs were lower than that of triolein-SPMDs, the concentrations of PAHs enriched in IL were high enough for detection. For the estimated concentrations of PAHs in water (Table 5), although the values for IL-SPMD method were also lower than those for triolein-SPMD method, they were close to each other at all sampling sites.

Our result also indicated that the samples from site 2 (industrial park) contained the highest levels of PAHs probably due to concentrative outlet of contaminants at this site and those from site 3 (Bapan canyon, located in upstream of the River) had the lowest levels of PAHs. The average concentrations of containments in water based on SPMDs residues will likely be a better representation of true concentration in nature (Luellen and Shea, 2002).

4. Conclusion

The study developed ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6])–containing semipermeable membrane sampler (IL-SPMD) to monitor polycyclic aromatic hydrocarbons in water. The method may avoid using harmful organic solvents without complex sample pretreatment. A good fit of mathematical models to the kinetic data was obtained

for all the studied PAHs through laboratory study. A preliminary field study indicated that IL-SPMD is potentially useful for contaminant monitoring in field.

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