

Short communication

Concentration of polyaromatic hydrocarbons in water to sodium dodecyl sulfate- γ -alumina admicelle

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Abstract

Polyaromatic hydrocarbons (PAHs) in water were concentrated into sodium dodecyl sulfate (SDS)- γ -alumina and di-2-ethylhexyl sodium sulfosuccinate (Aerosol-OT, AOT)- γ -alumina admicelles. The comparison of the binding constants ($K_{ad} = \frac{\text{adsorbed concentration of the solute (mol/g surfactant)}}{\text{the concentration in the bulk aqueous phase (mol/ml)}}$) indicated almost the same extraction abilities of the both admicelles. However, better and more reproducible recovery was obtained in the concentration of PAHs into the SDS- γ -alumina admicelle. PAHs in tobacco smoke that were trapped in water were successfully concentrated into SDS- γ -alumina admicelle for the HPLC analysis. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Polyaromatic hydrocarbons (PAHs) are omnipresent environmental pollutants resulting from combustion, crematory, automobile exhaust. The methods for concentrating these compounds prior to their analysis were solvent extraction and extensive sample cleanup procedures. However, the solvent extraction methods often use considerable amounts of organic solvents, which can generate serious problems with respect to human health and ecological systems.

Recently, we have designed a method for concentrating traces of hydrophobic analytes including organic compounds and metal chelates in water samples using surfactant-coated solid materials as extraction media [1–4]. Surfactant molecules cooperatively sorb on solid surfaces by electrostatic and hydrophobic forces and, thus, form aggregates namely hemimicelle or admicelle [5–7]. Several types of admicelles can be prepared just by mixing solid materials and appropriate surfactants in the aqueous solution. Their applications to the collection or the separation of hydrophobic compounds have been increasingly performed [3–9].

In the present study, the admicelle-mediated extraction method was applied to the concentration of PAHs in water sample. The extraction abilities of sodium dodecyl sulfate (SDS)- γ -alumina and di-2-ethylhexyl sodium sulfosuccinate (Aerosol-OT, AOT)- γ -alumina admicelles were compared in order to clarifying appropriate system for concentrating PAHs prior to their HPLC analysis. The method was applied to the concentration of PAHs in a water sample containing tobacco smoke.

2. Experimental

2.1. Reagents

Alumina (γ -form, 10–50 μm , for column chromatography) was obtained from Katayama (Osaka, Japan). A Bond Elut Jr. ALA cartridge column (Varian, Palo Alto, CA, USA), being filled with 500 mg of alumina, was employed. SDS (for biochemistry) and AOT were purchased from Wako (Tokyo, Japan) and Nakarai Tesque (Kyoto, Japan), respectively. PAHs; phenanthrene, fluoranthene, pyrene, benz[a]anthracene, benzo[k]fluoranthene, perylene, benzo[a]pyrene, and benzo[ghi]perylene, were obtained from

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Tokyo Kasei (Tokyo, Japan). Other reagents used were of analytical grade. The water employed was prepared using a Milli-Q Gradient water system (Millipore, Milford, MA, USA).

2.2. Concentration of PAHs in water containing tobacco smoke

Tobacco side-stream smoke caused from tithe of cigarette was collected by the suction through 200 ml of 1 mM nitric acid. The resulting solution was passed through the Bond Elut Jr. onto which 33 mg of SDS had been precedently sorbed. PAHs collected were eluted with 1-ml of acetonitrile. A 20 μ L aliquot of the supernatant were injected into HPLC system, which was composed of a Jasco (Tokyo, Japan) PU-980 intelligent pump, a UV-970 intelligent ultra-violet detector, and an 807-IT integrator.

3. Results and discussion

3.1. Extractability of polyaromatic hydrocarbons

Table 1 summarizes the collection yields of series of organic compounds including PAHs onto SDS- and AOT- γ -alumina admicelles under the prescribed conditions. The extent of the collection seems to increase with increasing hydrophobic properties of the solutes. When the extent of collection is represented by binding constant, K_{ad} [6,7], of a solute to SDS or AOT molecules in admicelles, it was independent of the amount of surfactant in the range from 25 to 150 mg. As shown in Fig. 1, there are linear relationship between the binding constant and aqueous-octanol distribution constant, $K_{o/w}$, being the measure of hydrophobic property of a compound [12,13]. This fact indicates that hydrophobic interaction predominantly contributes to solute collection.

Table 1
Recoveries of hydrophobic organic compounds, $\log K_{ad}$, and $\log K_{o/w}$

Compound	SDS (mg)	Sorbed (%)	$\log K_{ad}$	AOT (mg)	Sorbed (%)	$\log K_{ad}$	$\log K_{o/w}$
Chlorophenol							
2-Chlorophenol	100	23 \pm 3	2.16				2.17 ^a
	150	30 \pm 4	2.14	150	28 \pm 2	2.10	
2,4-Dichlorophenol	25	27 \pm 3	2.85				3.21 ^a
	100	63 \pm 4	2.92				
2,3,4-Trichlorophenol	150	66 \pm 7	2.82	150	81 \pm 2	3.17	
	25	66 \pm 2	3.59	25	69 \pm 5	3.65	3.80 ^a
2,3,4,6-Tetrachlorophenol	100	86 \pm 4	3.45	150	>98		
	25	81 \pm 4	3.94	25	78 \pm 3	3.85	4.42 ^a
Pentachlorophenol	100	>98		150	>98		
	10	76 \pm 2	4.20				5.12 ^b
	25	84 \pm 2	4.04	25	88 \pm 3	4.19	
	100	>98		150	>98		
Phthalate esters							
Dimethylphthalate	100	47 \pm 5	2.64				1.56 ^c
	150	49 \pm 3	2.51	150	38 \pm 2	2.31	
Diethylphthalate	25	49 \pm 2	3.28	25	7 \pm 2		2.47 ^c
	100	84 \pm 1					
Dibutylphthalate	150	86 \pm 1		150	49 \pm 3	2.51	
	25	89 \pm 2	4.22	25	81 \pm 2	4.25	4.72 ^c
	100	96 \pm 1					
	150	>98		150	98 \pm 1		
Polyaromatic hydrocarbon							
Naphthalene	25	49 \pm 7	3.28				3.35 ^c
	100	76 \pm 4	3.21				
Phenanthrene	25	94 \pm 1	4.48	25	81 \pm 4	3.94	4.52 ^c
	100	98 \pm 1		150	97 \pm 2		
Fluoranthene	25	90 \pm 1	4.24	25	79 \pm 5	3.90	5.20 ^c
	100	98 \pm 1		150	97 \pm 2		
Pyrene	100	97 \pm 1	4.18	150	93 \pm 3		5.00 ^c
Benz[a]anthracene	10	95 \pm 1	4.97				5.91 ^c
	100	>98					
Benzo[k]fluorancene	100	>98					6.63 ^c
Benzo[a]pyrene	100	>98					6.35 ^c
Benzo[ghi]perylene	100	>98					6.90 ^c

Average of three experiments, γ -alumina: 1.5 g, solution volume: 50 ml, pH 2, 25 \pm 1 $^{\circ}$ C

^a Ref. [10].

^b Ref. [11].

^c Ref. [12].

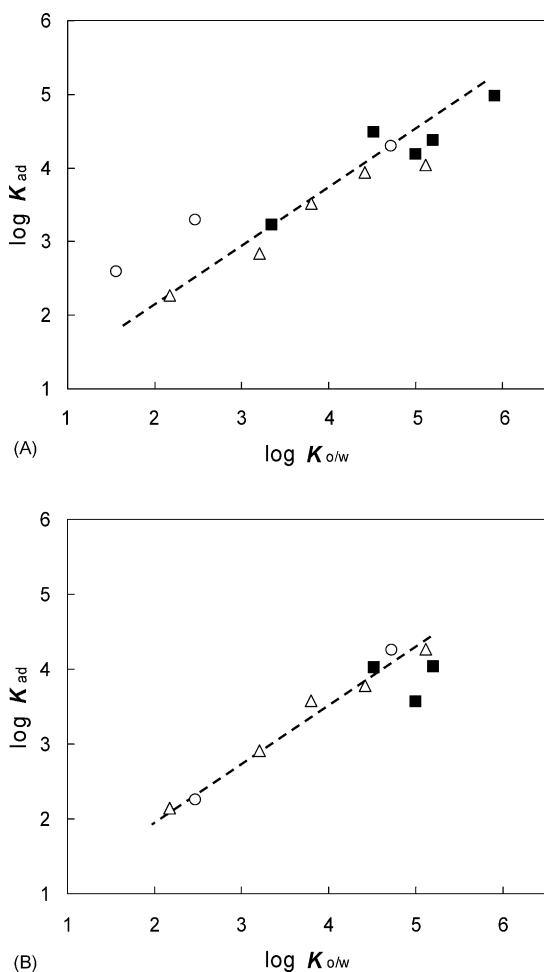


Fig. 1. Correlations between logarithmic binding constant ($\log K_{ad}$) and logarithmic aqueous-octanol distribution coefficient ($\log K_{o/w}$) of chlorophenol (Δ), phthalate ester (\circ), and polyaromatic hydrocarbon (\blacksquare). (A) SDS- γ -alumina admicelle, (B) AOT- γ -alumina admicelle.

Previously, we reported that AOT admicelle had greater hydrophobicity than SDS admicelle has and, therefore, seemed to be superior as a collecting medium for hydrophobic analyte [4]. However, almost the same profiles of the correlation in Fig. 1 indicate similar extraction abilities of the both admicelles. The recoveries of phenanthrene, fluoranthene, and pyrene to AOT admicelle were rather insufficient and less reproducible. The reason is unclear but may be ascribed to the difference in the specific volume of the admicelle. SDS molecule has longer alkyl moiety than AOT has. Additionally, the aggregation number of AOT (12–16 [14,15]) is smaller than that of SDS (50–62 [16,17]). Volume constraint effect encountered in the solute distribution in normal micellar system [18] may also work in the incorporation of bulky PAHs into AOT admicelle. Thus, SDS- γ -alumina admicelle was selected for concentrating PAHs.

3.2. Application to tobacco smoke analysis

A successful application of admicelle-mediated extraction was shown in Fig. 2. When the sample solution containing the

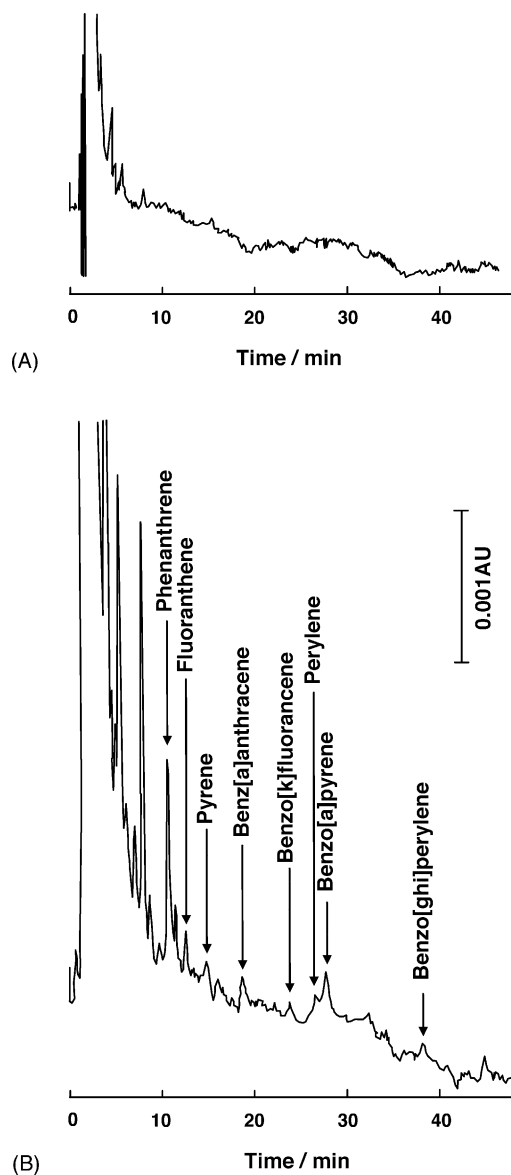


Fig. 2. Chromatograms of organic pollutants in tobacco smoke sample without concentration (A) and with admicelle-mediated extraction (B). Column: Mightysil RP-18-GP ($5\ \mu\text{m}$) 150 mm \times 4.6 mm, mobile phase: 60% (v/v) aqueous acetonitrile, flow rate: 1 ml min^{-1} , detection wavelength: 254 nm.

components in tobacco smoke was injected, no distinct peaks were observed (Fig. 2A). In contrast, some apparent peaks of polyaromatic hydrocarbons were observed after 200-fold concentration by admicelle-mediated extraction (Fig. 2B). The result indicates that the present method is useful for concentrating trace PAHs in water samples prior to the HPLC analysis. The combination to their fluorescent detection would be promising for the application to the analyses of air or fuel exhausts.

4. Conclusion

The binding constants of PAHs in SDS- and AOT- γ -alumina admicellar systems indicates almost the same

extraction ability of the both admicelles. However, better recovery of PAHs and its reproducibility were obtained in the latter system, suggesting better compatibility of SDS- γ -alumina admicelle for the collection of PAHs. The combination of aeration and admicelle-mediated extraction would be useful for analyzing organic contaminants in air or exhaust.

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