

Aerosol-OT- γ -alumina admicelles for the concentration of hydrophobic organic compounds in water

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Abstract

A novel admicelle composing of a dialkylated anionic surfactant, di-2-ethylhexyl sodium sulfosuccinate (Aerosol-OT, AOT) and γ -alumina was prepared by mixing them in acidic aqueous solution. The amount of the maximum sorption of AOT on 1 g of alumina at pH 2 was ca. 130 mg. By comparing the fluorescence spectra of *N*-phenyl-1-naphthylamine in different solvents, the solvent property of AOT- γ -alumina admicelles was corresponding to that of toluene or diethyl ether. Thus, the AOT- γ -alumina admicelles had greater hydrophobicity than SDS- γ -alumina admicelles having similar hydrophobicity to 1-octanol or ethyl acetate. Hydrophobic organic compounds, chlorophenols having more than three chloro substituents, octylphenol, nonylphenol, dibutyl phthalate was almost quantitatively (98% or more) collected onto AOT admicelles composing of 1.5 g γ -alumina and 150 mg AOT. The greater collection yields rather than those in SDS-admicellar system were ascribable to greater hydrophobicity and stability of AOT admicelles. After the 500-fold concentration, traces (nM) of organic contaminants in water samples were successfully detected with an HPLC having a photometric detector.

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1. Introduction

Surfactant molecules tend to aggregate and thus form micelles that can incorporate hydrophobic compounds in the aqueous solutions. Such properties of the surfactant micelles have been extensively used as the separation media for several efficient extraction methodologies including cloud-point extraction and micelle-enhanced ultrafiltration [1–6]. However, micelles are extremely small and hence have difficulties in the separation from the bulk aqueous solution. Additionally, viscous properties of concentrated micellar solutions significantly reduce the efficiency in concentration and the easiness in manipulation of these micelle-mediated separation techniques. On the other hand, micelle-like surfactant aggregates sorbed on solid materials (namely hemi-micelle or admicelle) seem to be a good alternative, because of the ability for easy and rapid fractionation from bulk aqueous solutions. The collection of ad-

micelles or the adsolubilization of some hydrophobic compounds has been investigated in the area of water treatment [7–12].

Recently, we established a concentration method in the basis of the sorption of hydrophobic metal chelates onto admicelles, in which negatively charged sodium dodecyl sulfate (SDS) molecules cooperatively adsorb and aggregate onto positively charged γ -alumina surfaces in weakly acidic media [13–19]. Traces of hydrophobic metal chelates in water were efficiently incorporated into the hydrophobic media provided by the admicelles. On the other hand, organic compounds were often insufficiently collected, because of their less hydrophobicity than very hydrophobic metal chelates [20,21].

In the present study, a novel admicelle, composed of Aerosol-OT (AOT) and γ -alumina, was prepared for improving the collection ability of organic compounds. The properties of the AOT- γ -alumina admicelles as the extracting solvents were evaluated on the basis of the fluorescence spectra of a probe molecule being responsible to the hydrophobicity of a solvent. Furthermore, the collection yields of some organic compounds were compared with those in

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SDS- γ -alumina admicelles. The compatibility of the novel admicelles to HPLC analysis was investigated.

2. Experimental

2.1. Chemicals and materials

Alumina (γ -form, 10–50 μm , for column chromatography, Katayama Chemicals, Osaka, Japan) was ultrasonically washed with 1 M nitric acid for 3 min and thoroughly rinsed with water. A Bond Elut Jr. Al-A cartridge column (alumina, acidic, Varian, Harbor City, CA, USA), being filled with 500 mg of alumina, was employed after rinsing with 50 ml of 0.01 M nitric acid. Di-2-ethylhexyl sodium sulfosuccinate (for water analysis, Aerosol-OT, AOT, Nakarai Tesque, Kyoto, Japan) was used as 5% (w/v) aqueous solution. The accurate concentration of AOT was determined by toluidine blue titration method [22]. A fluorescence molecular probe, *N*-phenyl-1-naphthylamine (PN), was obtained from Funakoshi (Tokyo, Japan). Sodium tetradecane sulfonate (STS), sodium hexadecane sulfonate (SHS), 2,4-dichlorophenol, 2,3,4-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol, diethyl phthalate, dibutyl phthalate, and di(2-ethylhexyl) phthalate were purchased from Tokyo Kasei (Tokyo, Japan). 4-Nonylphenol, 4-octylphenol, and 4-octylphenol monoethoxylate were obtained from Kanto Chemical (Tokyo, Japan). The stock solutions of these analytes were prepared as 1 mM ethanol solutions. Other reagents used were of analytical grade. The water employed was prepared using a Millipore (Milford, MA, USA) Milli-Q SP reagent water system.

2.2. Fluorescence measurement of PN in admicellar solutions

The fluorescence measurement was performed by the manner that had been previously reported for the evaluation of the hydrophobic property of SDS- γ -alumina admicelles [23]. To obtain fine particles that can be stably dispersed in the aqueous solution, γ -alumina was soaked in water and then ground in an alumina mortar. After the suspension was passed through 0.4 μm membrane filter, the filtrate was freeze-dried. The aqueous solution (pH 4 buffered with 0.01 M acetate) containing 0.1% (w/v) alumina, 1 mM of AOT, and 1 μM of PN was placed in a 1 cm quartz cell. The fluorescence spectrum of PN was measured with a Perkin-Elmer LS-50B luminescence spectrometer at 25 °C. The bandwidths of the excitation and emission were 5 nm.

2.3. Batch extraction

To prepare admicelles, an aqueous solution containing 0–200 mg of AOT was added to an aqueous suspension of 1.5 g γ -alumina with gentle mixing. The solution pH was

adjusted to 2.0 with nitric acid. Total volume of the solution system was 50 ml. To the admicelle system, 50 μl ethanol solution containing 1 mM analytes was added. After the solution was shaken for 5 min, a 20- μl 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. The mobile phase composition and detection wavelength were 60% (v/v) aqueous acetonitrile and 280 nm for chlorophenols, while 80% (v/v) aqueous acetonitrile and 290 nm were used for alkylphenols and phthalate esters.

2.4. Concentration to admicelle filled column

To prepare an admicelle column, 50 ml of 0.01 M nitric acid containing 50 mg of AOT was passed through a Bond Elut Jr. cartridge column filling with 500 mg of alumina. River water sampled from Shonai River (Nagoya, Japan) was centrifuged at 15 000 rpm for 30 min in order to remove suspended solids. The sample solution (500 ml) was adjusted to pH 2 by adding 0.4 ml of concentrated nitric acid. Injecting the sample solution to the column with a glass syringe performed sample loading. After washing the column with 50 ml Milli-Q water, analytes were eluted with 1.0 ml acetonitrile. A 20- μl aliquot of the eluate was injected to the HPLC system, in which the operating conditions were the same as those described above.

3. Results and discussion

3.1. Formation of alumina-based admicelles

Anionic surfactant molecules are expected to effectively be sorbed on positively charged γ -alumina surfaces in slightly acidic solutions [24,25]. Among the anionic surfactants, SDS was accepted as the most promising for preparing admicelles that can be used for collecting hydrophobic solutes from water [7,8,10–21]. Similarly to chemically bonded alkylsilane moieties, cooperatively sorbed SDS molecules provide hydrophobic environment on alumina surfaces [26]. Based on the fluorescence spectrum of PN, being a molecular probe in which the spectrum is responsive to solvent polarity, the hydrophobic property of SDS- γ -alumina admicelle was corresponding to 1-octanol or ethyl acetate [23]. The ability in the collecting hydrophobic compounds is ascribable to the hydrophobic property of the admicelles. Selecting more hydrophobic surfactants than SDS may increase the hydrophobicity of admicelles.

SHS and STS might be good choice because they have longer alkyl-substituents and thus provide more hydrophobic media than SDS does. However, because of their very low solubilities at room temperature, the solutions had to be warmed to 50 °C for preparing the admicelles. Furthermore, the amounts of their sorption were considerably lower than the case of SDS, when the solutions were cooled to room

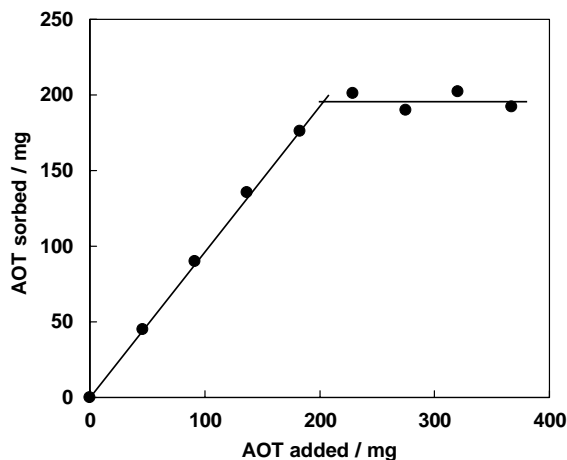


Fig. 1. Sorption of AOT on 1.5 g γ -alumina at pH 2.

temperature. Solubilization of surfactant molecules was essential for the admicelle formation.

An attractive alternative is AOT having a couple of branched alkyl-moieties. Because of its good solubility to apolar organic solvents, AOT is often utilized to form reversed micelles or water-in-oil microemulsions [26–28] to incorporate hydrophilic solutes in organic solvents [29–31]. On the other hand, it has also been used for preparing normal micelles in water due to its considerable solubility in water [32–34]. Thus, AOT seems the most promising surfactant for preparing admicelles having highly hydrophobic property.

Various amounts of AOT were mixed with 1.5 g of γ -alumina at pH 2 to measure sorption capacity of alumina. The amount of the sorbed was estimated from the determination of AOT in the supernatant by the toluidine blue titration method [22]. As shown in Fig. 1, up to ca. 200 mg of AOT was quantitatively sorbed on the alumina.

On the other hand, the amount of AOT sorption was constant in the further addition of AOT. These results indicate the formation of very stable admicelles.

3.2. Solvent property of AOT–alumina admicelles

Comparing spectral signals of certain molecular probes has extensively been performed for evaluating the solvent properties of micelles or admicelles. As reported previously, PN was a good fluorescent probe molecule for evaluating solvent property of γ -alumina-based admicelles [23]. Table 1 summarizes the maximum wavelengths (λ_{\max}) of the excitation and the emission of PN in some organic solvents as well as solvent parameters. As found in the previous study, SDS– γ -alumina admicelles have similar polarity to 1-octanol or ethyl acetate and more hydrophobic property than SDS micelles have. The highly hydrophobic property of the admicelles rather than normal micelles was explained by difference in the aggregating situation of the surfactant molecules. In the normal micelles, negatively charged head groups electrostatically repel and hydrated by large amounts of water [37]. On the other hand, the negatively charged head groups can be neutralized by the positively charged γ -alumina surfaces in the admicelles. Thus, the surfactant molecules must densely aggregate and lose hydrated water.

On the basis of the λ_{\max} value of PN, AOT– γ -alumina admicelles were hydrophobic rather than SDS– γ -alumina admicelles. The solvent property of the AOT admicelles was corresponding to those of toluene or benzene. Such extreme hydrophobicity may be caused by the combination of the hydrophobicity of AOT and their dehydration by the sorption on positively charged γ -alumina surfaces. Highly hydrophobic property of AOT admicelles would be advantageous for the efficient collection of analytes.

Table 1
Spectral data of PN in some solvents and their solvent parameters

Solvent	$\lambda_{\max, \text{excitation}}$ (nm)	$\lambda_{\max, \text{emission}}$ (nm)	Dielectric constant ^a	δ^b (cal mol ⁻¹ cm ⁻³) ^{1/2}
Water	328.0	452.0	78.54	23.53
Acetonitrile	339.3	424.0	32.6	12.11
Methanol	340.0	419.3	36.0	14.50
Ethanol	341.0	417.0	24.3	12.78
1-Propanol	342.0	415.5	20.4	12.18
1-Butanol	340.7	413.9	16.1	11.60
1-Octanol	343.0	411.0	10.4	–
Ethyl acetate	341.0	408.0	6.11	8.91
Toluene	340.0	395.5	2.36	8.93
Benzene	340.0	395.0	2.28	9.16
SDS micelle ^c	340.0	432.5		
SDS– γ -alumina admicelle ^{c,d}	341.0	409.0		
AOT micelle	341.3	407.0		
AOT– γ -alumina admicelle ^d	341.7	395.2		

^a At 25 °C [35].

^b δ : solubility parameter (25 °C) [36], 1 cal = 4.184 J.

^c Ref. [23].

^d 0.01% (w/v) γ -alumina.

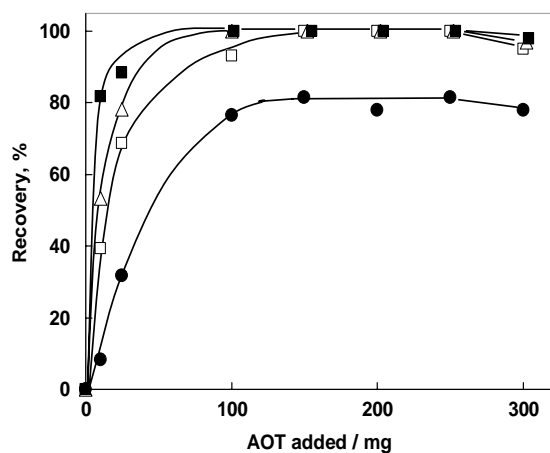


Fig. 2. Effect of the amount of AOT on the collection of 1 μ M chlorophenols to 1.5 g γ -alumina at pH 2: (●) 2,4-dichlorophenol, (□) 2,3,4-trichlorophenol, (△) 2,3,4,6-tetrachlorophenol, (■) pentachlorophenol.

3.3. Collection of hydrophobic organic compounds

Similarly to the SDS- γ -alumina admicellar system, the collection yields of chlorophenols onto γ -alumina remarkably increased with increasing the amount of AOT (Fig. 2), due to the increasing formation of hydrophobic AOT admicelles. The maximum collection yields of the respective chlorophenols were obtained in the range of 100–200 mg AOT for 1.5 g of γ -alumina. The slight decrease by the addition of further amount of AOT can be attributed to the saturation of AOT sorption and hence by the distribution of the solute to the normal AOT micelles formed in the bulk aqueous solution. In the present study, the optimum amount of AOT chosen was 150 mg for 1.5 g of γ -alumina.

The collection yields of some hydrophobic compounds including chlorophenols, alkylphenols, and phthalate esters were listed in Table 2. The yields seem to be dependent on their hydrophobic properties that are represented by octanol–water distribution coefficient ($K_{o/w}$). This indicates that the hydrophobic interaction was predominant factor for the incorporation of solutes. Because of their less hydrophobic properties, 2-chlorophenol, dimethyl phthalate, and diethyl phthalate was less extractable. On the other hand, chlorophenols having more than three chloro substituents, alkylphenols, dibutyl phthalate, and di(2-ethylhexyl) phthalate were sufficiently collected.

Table 3 lists the yields of the collection and the elution of chlorophenols when the columns filling with SDS–alumina or AOT–alumina admicelles were employed for collecting them in 50-ml aliquot of aqueous solution. Here, the amount of surfactant to be loaded to 500 mg of alumina (Bond Elut Jr.) was set to 50 mg, because of the equivalent AOT/ γ -alumina ratio (150 mg/1.5 g) on comparing with the batch experiment. Trichlorophenol that had been insufficiently collected on SDS admicelles was quantitatively sorbed on AOT admicelles.

Table 2
Recovery of hydrophobic organic compounds to AOT admicelles^a

Compound	AOT (mg)	Recovery (%)	log $K_{o/w}$
2-Chlorophenol	150	27.7 \pm 0.9	2.15 ^b
2,4-Dichlorophenol	150	81.5 \pm 0.4	3.08 ^c
2,3,4-Trichlorophenol	25	68.8 \pm 4.3	3.69 ^c
	150	>99	
2,3,4,6-Tetrachlorophenol	25	78.2 \pm 3.7	4.10 ^c
	150	>99	
Pentachlorophenol	25	88.3 \pm 2.0	5.12 ^c
	150	>99	
4- <i>tert</i> -Octylphenol	25	94.9 \pm 0.6	4.12 ^d
	150	>99	
4- <i>n</i> -Nonylphenol	25	91.0 \pm 1.1	4.48 ^d
4- <i>n</i> -Nonylphenol ethoxylate	25	93.0 \pm 0.8	~4.2 ^d
Dimethyl phthalate	150	38.1 \pm 0.3	1.56 ^b
Diethyl phthalate	150	49.5 \pm 0.6	2.47 ^b
Dibutyl phthalate	25	90.0 \pm 1.0	4.72 ^b
	150	97.8 \pm 0.2	
Di(2-ethylhexyl) phthalate	150	>99	

^a γ -Alumina: 1.5 g, $n = 3$.

^b Ref. [38].

^c Ref. [39].

^d Ref. [40].

Table 3 also indicates that the efficiency of the elution was considerably improved in the AOT admicelles. This may be attributed to the excellent compatibility of AOT to hydro-organic solvents. SDS is highly water-soluble but less soluble in polar organic solvents such as ethanol or acetonitrile. SDS molecules sorbing on alumina surfaces may coagulate and hence engage solutes during the elution with acetonitrile. In contrast, AOT molecules on the surfaces seem to highly solvate with either aqueous or organic solvent and, hence, are expected to have remarkable fluidity through collecting and eluting procedures. Such property of AOT admicelles would be advantageous for efficient pre-concentration of analytes.

3.4. Sample loading capacity of AOT-admicellar cartridge

In order to clarify the limitation of the sample loading volume, increasing volumes of acidic solution (pH 2)

Table 3
The yields (%) of collection and elution of chlorophenols

	SDS admicelles ^a		AOT admicelles ^a	
	Collection	Collection and elution	Collection	Collection and elution
Trichlorophenol	89 \pm 4	81 \pm 5	100	96 \pm 6
Tetrachlorophenol	100	77 \pm 6	100	98 \pm 4
Pentachlorophenol	100	70 \pm 10	100	86 \pm 10

^a Surfactant: 50 mg, γ -alumina: 500 mg, sample volume: 50 ml, eluting volume: 1 ml, concentration of each chlorophenol: 1 μ M, $n = 3$.

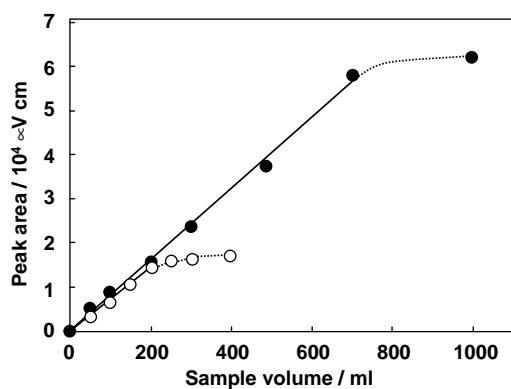


Fig. 3. Effect of sample volume on the peak area for 0.1 μM of 4-nonylphenol in the chromatogram: (○) SDS- γ -alumina admicelles, (●) AOT- γ -alumina admicelles.

containing 0.1 μM of 4-nonylphenol were passed through the admicelle column. In the SDS- γ -alumina admicelle column, the curve of the peak area in chromatogram that obtained by the injection of the eluate from the admicelles as a function of the sample loading volume was straight up to 200 ml of sample volume (Fig. 3). At greater sample volumes, the slope of the curve gradually lowered, being ascribable to the insufficient recovery. This may be attributed to the release of SDS molecules from the alumina support. This limits the sample loading capacity of SDS-admicelle column.

On the other hand, the collection of 4-nonylphenol was quantitative up to 700 ml of sample loading to the AOT- γ -alumina admicelle column (Fig. 3). This may be explained by the stability of AOT admicelles rather than SDS admicelles. The critical micelle concentration of AOT (ca. 2.5 mM [41–43]) is less than that of SDS (8.1 mM [44]). Additionally, the turbid property of the aqueous solutions of concentrated AOT suggested the formation of larger aggregates in the higher concentration range, although the aggregation number of AOT (12–16 [42,43]) is less than that of SDS (ca. 62 [44]). Since the surfactant molecules sorb and, thus, are concentrated on γ -alumina surfaces, AOT may form aggregates larger than the case of SDS admicelles. Additionally, the difference in the structure of surfactant could also affect the formation and stability of admicelles. AOT molecule having two ester moieties may be expedient for the cooperative sorption on γ -alumina surfaces.

3.5. Application to water samples

An application of the present method to the 500-fold concentration of analytes for the HPLC analysis is shown in Fig. 4. When a river water sample spiked with 1 nM of 2,3,4-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol was directly injected to the HPLC system, no peaks appeared in the chromatogram (A). In contrast, three apparent peaks were observed (B) after 500-fold

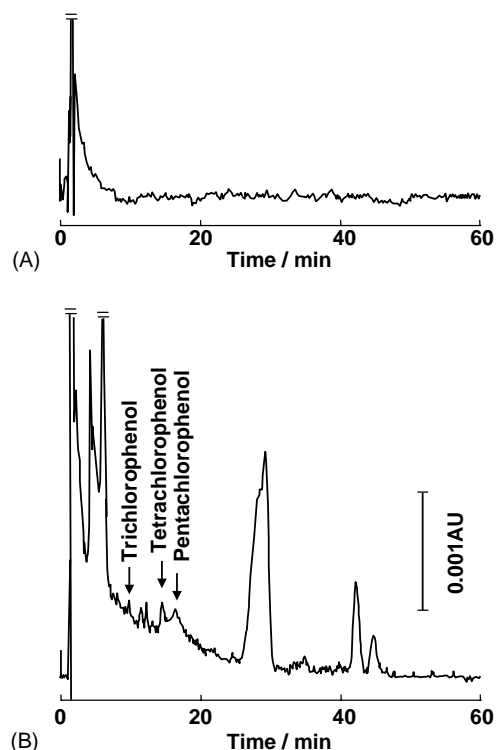


Fig. 4. Chromatograms of river water to which 1 nM 2,3,4-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol were spiked: (A) without concentration; (B) with admicelle-mediated extraction. Column, Mightysil RP-18-GP (5 μm) 150 mm \times 4.6 mm; mobile phase, 60% (v/v) aqueous acetonitrile; flow-rate, 1.0 ml min^{-1} ; detection wavelength, 290 nm.

concentration. Linear relationships between peak areas and concentrations were obtained for these chlorophenols in the concentration range of 5–100 nM. This indicates the potential of the present method for determining these compounds at trace ($\mu\text{g l}^{-1}$) levels.

The present method was also applied to the detection of organic contaminants in distilled water. There were no peaks in the chromatogram by direct injection of distilled water (Fig. 5A). On the other hand, some apparent peaks were observed as a result of 500-fold concentration (Fig. 5B). Fig. 5C shows the chromatogram obtained by the introduction of the 500-fold concentrated sample that 2 nM each of dibutyl phthalate, 4-octylphenol, 4-nonylphenol, and 4-nonylphenol monoethoxylate had been spiked into the distilled water. A huge peak of dibutylphthalate and other many peaks are ascribable to the eluted contaminants from a polyethylene container or the components that had existed in feed water. The results obtained in the present study indicate the availability of AOT admicelles for the concentration of trace organic contaminants prior to their HPLC analysis.

Finally, AOT- γ -alumina admicelles are favorable to the commercially available polymer based solid materials or hydrophobically modified silica gels [45–47]. They are chemically stable and, hence, seem to be advantageous for

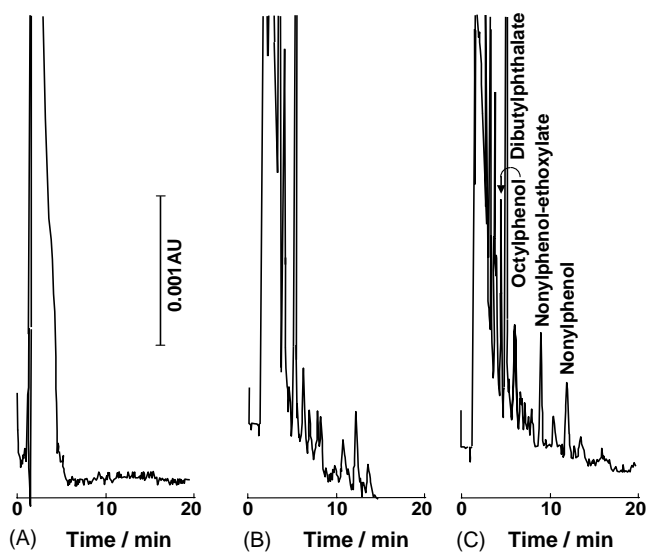


Fig. 5. Chromatograms of distilled water: (A) without concentration; (B) with admicelle-mediated extraction; (C) with admicelle-mediated extraction of the sample to which 2 nM of dibutylphthalate, 4-*tert*-octylphenol, 4-nonylphenol, and 4-nonylphenol monoethoxyate were spiked. Mobile phase, 80% (v/v) aqueous acetonitrile; detection wavelength, 280 nm; other conditions were the same as Fig. 4.

loading large volume of water sample. However, low water permeability of these materials results in slow mass transfer between bulk aqueous solution and the solid. Therefore, a limited flow rate of water through the solid-phase extraction cartridge (typically 10–20 ml min⁻¹) lengthens the sample loading time [48,49]. In contrast, because of the excellent water permeability of the admicelles, a higher flow rate (higher than 60 ml min⁻¹) could be applied for sample loading. This is particularly advantageous when large quantities of sample have to be loaded to the admicelle-filled cartridge column.

4. Conclusion

AOT- γ -alumina admicelles were successfully prepared just by mixing γ -alumina and AOT in weakly acidic aqueous solutions. They were useful for concentrating hydrophobic organic compounds in water. The collection of hydrophobic compounds was ascribable to the hydrophobic solvent property of the admicelles corresponding to benzene or toluene. The yields of the collection and the elution were improved comparing with those in the conventional SDS- γ -alumina admicellar system. Large sample loading capacity of AOT- γ -alumina admicelles enables highly efficient concentration of trace analytes. The ability for concentrating hydrophobic compounds would greatly extend the feasibility to apply the admicelle-mediated separation method to several hydrophobic organic contaminants in a variety of water samples.

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