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Concentration of nonylphenol and its polyethoxylated derivatives by polymer-mediated extraction

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Abstract

Polymer-mediated extraction based on thermoresponsive precipitation of poly(*N*-isopropylacrylamide) [PNIPAAm] was applied to the concentration of amphiphilic compounds, nonylphenyl polyethoxylates (NPnEOs), in water. Among these nonionic surfactants, NPnEOs possessing the number, n, of ethoxy unit less than 5 were quantitatively recovered in polymer precipitates when a 0.100-g portion of PNIPAAm was used for a 10 ml sample solution. Torelance limit (30 ppm) against a typical industrial anionic surfactant, sodium dodecylsulfate, strongly suggests the potential to use the present method for practical purposes. After preconcentration, trace nonylphenol and mono-ethoxylated nonylphenol (ppb-level) in a river water sample were successfully determined by high-performance liquid chromatography with ultra-violet photometric detection.

Keywords: Nonylphenol; Polyethothylate; *N*-isopropylacrylamide

1. Introduction

Polyethoxylated nonylphenols (NPnEOs) are well known synthetic detergents which have been extensively used in pulp, paper, and textile industries [1]. However, recent reports of estrogenicity as well as the toxicity and persistence of their degradation products such as nonylphenol, mono- or di-ethoxylated nonylphenyl ethers, and some oxidized derivatives [2–4] indicate to us the requirement of a simple, rapid and highly sensitive method for monitoring these compounds.

NPnEOs in water had been pre-concentrated by a solvent subilation, steam distillation, or liquid–liquid extraction prior to chromatographic analysis [5–8]. However, these methods tend to be avoided because of cumbersome and time consuming procedures. The requirement of large amounts of volatile and toxic organic solvents is also the reason for eliminating liquid–liquid extraction methodology. Recently, solid-phase extraction techniques using several types of solid materials have been employed for concentrating NPnEOs or other polyethoxylated surfactants [9–12]. The surfactants adsorbed to the solid materials can be eluted by sequential washing with some suitable organic solvents. Despite extensive applications of the solid-phase extraction, the recovery and reproducibility in the elution of alkylphenolic surfac-

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tants from the solid materials are often insufficient, probably due to very strong interaction of alkylphenolic moiety of the surfactants with the solid materials.

Recently, we developed a new extraction methodology (polymer-mediated extraction) based on the thermoresponsive precipitation of a water-soluble polymer; poly(*N*-isopropylacrylamide) [PNIPAAm] or polyvinylmethyl ether, for concentrating hydrophobic analytes in water [13–20]. That is, in an aqueous thermoresponsive polymer solution, any hydrophobic compounds present will be solubilized and incorporated into the thermoresponsive polymer assembly. When the solution is warmed, solubilized polymers become water-insoluble and, then, form condensed polymer precipitates (polymer phase) having an extremely small volume. Since the polymer aggregation is rapid and quantitative, hydrophobic compounds in the aqueous solution are efficiently concentrated into the polymer phase. A number of compounds including polyaromatic hydrocarbons, alkylbenzenes, chlorobenzenes, chlorophenols, pesticides, steroid hormones, phospholipids, hydrophobic metal chelates, and ion-pairs were successfully concentrated [13–20].

An important advantage of the polymer-mediated extraction is the ability to concentrate a wide range of hydrophobic analytes with high-concentration factors by very simple and rapid procedures. Additionally, polymer aggregates can be directly introduced into the hygro-organic mobile phase of reversed-phase liquid chromatography after the aggregates are dissolved with small amounts or water or organic solvents [14,16]. Thus, the elution of analytes from the polymer assembly is not necessary. The concentrated polymer does not interfere with the stream of mobile phase or ultra-violet (UV) monitoring because of its good solubility in aqueous-acetonitrile and of very weak UV absorption. Therefore, the polymer-mediated extraction is potentially useful for concentrating polyethoxylated alkylphenols in environmental or waste water. However, there have been no studies about the application of the polymer-mediated extraction to surfactants having both of hydrophobic and hydrophilic moieties.

In this study, the feasibility of extending the polymer-mediated extraction to the concentration of amphiphilic compounds, polyethoxylated nolylphenols, in water was explored. The dependence of the recovery on the number of ethoxy units in these surfactant molecules was investigated for clarifying the limitation of this method. Furthermore, the method was applied to the determination of nonylphenols in river water.

2. Experimental

2.1. Reagents

A thermoresponsive polymer, PNIPAAm (average molecular weight: 125,000 by GPC (polystyrene standard)), was synthesized by aqueous redox polymerization of *N*-isopropylacrylamide, a generous gift from Kojin Co. Ltd. (Tokyo, Japan), with ammonium persulfate and *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine according to the method previously reported [16,21]. After repeated crystallization in 50% (v/v) aqueous ethanol, the polymer was freeze dried for obtaining sponge-like precipitates that can be rapidly dissolved in aqueous solutions. Standard reagents; 4-nonylphenol, 4-nonylphenol mono-ethoxylate, 4-nonylphenol di-ethoxylate, 4-nonylphenoxy acetic acid, dibutylphthalate, and bis(2-ethylhexyl)phthalate employing for peak identification were obtained from Kanto Chemical (Tokyo, Japan). Polyethoxylated nonylphenols NPnEO ($n=2$, 5, 7.5, 10, 15, and 20 where numericals indicate average number of ethoxy units) were purchased from Tokyo Kasei Co., Ltd. (Tokyo, Japan). The water used was prepared using a Milli-Q SP reagent water system from Millipore Corp. (Milford, MA, USA).

2.2. Polymer-mediated extraction of surfactant

A 10 ml sample water containing nonylphenol polyethoxylates was poured into a glass tube in which a 0.100 g PNIPAAm was placed. In case of river water, samples drawn from Kiyose river (Musashino area of Tokyo) were centrifuged at 3000 rpm for 30 min in order to remove floating sediments beforehand. After the polymer was completely dissolved, a 0.5-ml portion of 2 *M* sodium chloride were added to the tube in order to obtain quantitative recovery of polymer precipitates on heating the solution [16,17]. The tube was incubated at 40°C for

5 min and, then, was vigorously shaken for agglutinating polymer precipitates into a droplet which can be easily taken out. The droplet of gum-like polymer phase floating on the solution was taken with a Teflon™-coated stainless steel micro-spatula and then was dissolved using a prescribed amount of acetonitrile to obtain a 350 μl sample solution. A 20 μl-portion of the sample solution was collected using a 1700 Hamilton gas-tight micro-syringe and was directly injected into HPLC system, which was composed of a Jasco PU-980 intelligent pump, Jasco UV-970 intelligent UV-detector, and Jasco 807-IT integrator. A 30% (v/v) of aqueous-acetonitrile was used as a mobile phase. Wavelength employed for monitoring NPnEOs was 254 nm. The recoveries of the analytes were calculated from the amounts in bulk aqueous and polymer phases, where their volume fractions were estimated on the basis of the volume of condensed polymer phase [1.40 ml/g(dry polymer)] [18].

3. Results and discussion

3.1. Effect of polymer concentration

The amount of PNIPAAm to be added is the most important factor that influences the recoveries of analytes, because the analytes are distributed between bulk aqueous and hydrated polymer media depending on their hydrophobic properties [15,16]. As illustrated in Fig. 1, the recoveries of NP5EO and NP15EO into the polymer phase increased with increasing the amount of PNIPAAm. This reflects the increase in volume fraction of the polymer phase which can incorporate the analytes. When a 0.100-g portion of PNIPAAm was added to a 10 ml sample solution, NP5EO was quantitatively collected to the polymer phase formed by temperature-induced dehydration of PNIPAAm. The addition of further PNIPAAm lowered the concentration factors of analytes due to the increase in the volume for analyte distribution. In contrast, greater concentration factors were obtained when lower amounts of polymer were used. However, the recoveries of NPnEOs may largely be influenced by the presence of several coexistants in samples. The addition of 0.100 g polymer to a 10 ml sample solution was the most adequate for obtaining reproducible recovery and high concentration factor.

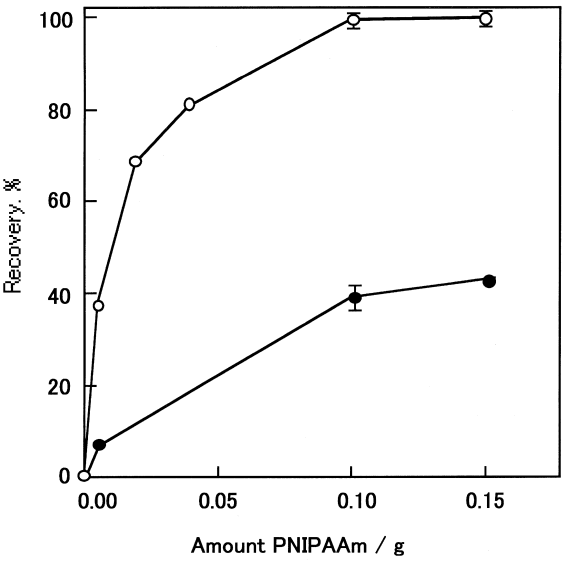

Fig. 1. Effect of polymer amount on NPnEO recovery. (○) NP5EO, (●) NP15EO. [NPnEO]=1.00×10^{-5} *M*. Error bar represents disperse of 5 runs. Point having no error bars is the average of triplicate runs.

3.2. Extractability of NPnEOs

Fig. 1 also shows that NP15EO having longer ethoxyl units is less extractable than NP5EO. For clarifying the limitation to apply the present method into the concentration of NPnEOs, the dependence of recovery on polyethoxy chain length was investigated. As illustrated in Fig. 2, NPnEOs having ethoxy units less than 5 were quantitatively recovered to polymer phase. On the other hand, the recovery of NPnEOs having longer ethoxy units than 5 decreased with increasing EO number. A large hydrophilic EO moiety in surfactant molecule increase the solubility in bulk aqueous solution and, hence, decrease the extractability to hydrophobic polymer phase. Although PNnEOs used in this study are not homogeneous, the tendency of extractability clarified here would almost indicate the limitation in the hydrophilic–lipophilic balance of surfactants which can deal with the polymer mediated extraction.

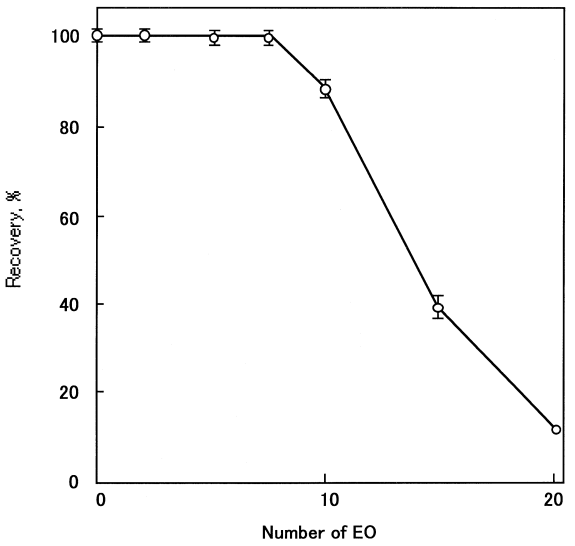

Fig. 2. Dependence of EO number on NPnEO recovery. [NPnEO]=1.00×10^{-5} *M*, PNIPAAm; 1.00% (w/v). Error bar represents disperse of 5 runs. Point having no error bars is the average of triplicate runs.

3.3. Effect of anionic surfactants

Anionic surfactants are often present in environmental or waste water samples in concentrations higher than nonionic surfactants [22,23]. Probably due to strong interaction of surfactant molecules with hydrophobic polymer assemblies, the anionic surfactants may significantly influence thermoresponsive properties of PNIPAAm. Indeed, thermoresponsive precipitation did not occur in the presence of a widely used synthetic anionic surfactant, sodium dodecylsulfate (SDS), above its critical micelle concentration (3 m*M* [24]). However, negligible interferences to the recoveries of NP, NP2EO, and NP5EO were observed at SDS concentrations up to 0.1 m*M* (ca. 30 mg l^{-1}). Since this tolerance limit could be far greater than the maximum conceivable concentration presenting in waste water after sewage treatment, the result obtained here indicates great potential to use polymer-mediated extraction for practical purposes.

3.4. Application to river water

A successful demonstration of the application of polymer-mediated extraction to HPLC analysis of nonylphenols in river water is shown in Fig. 3. When the supernatant of river water was directly injected to the HPLC system, no peaks were appeared in chromatogram (A). In contrast, some peaks were observed (B) when the sample was concentrated by polymer-mediated extraction. Among these peaks, two were successfully identified as NP1EO and NP by comparing the retention times of the standard reagents listed in the experimental section. Fig. 4 illustrates the calibration curves of them obtained by a standard addition method. The intercepts of the respective curves indicate that the concentrations of NP and NP1EO were 23 and 7 μg/l (ppb), respectively.

Finally, the present method can be comparable to solid-phase extraction (SPE) that has been extensively employed in the pre-concentration of nonylphenol surfactants and others [9–12]. SPE is known as a rapid and simple method for concentrating varieties of analytes in aqueous media. However, due to slow mass transfer between bulk aqueous solutions and solid materials, SPE often takes long time when large volume of sample solutions have to be treated. On the other hand, polymer-mediated extraction can rapidly concentrate analytes from large volume of a sample solution, because the analytes have been already incorporated into hydrated polymer media dispersing in the aqueous solutions before polymer precipitation [25].

Another advantage of the polymer-mediated extraction can be noticed is needlessness of elution procedure. Elution in SPE often increases sample volume and, hence, decrease concentration factor. Furthermore, strong interaction of analytes with solid-phase materials often causes insufficient recoveries of desired analytes. In contrast, elution procedures can be eliminated in the polymer-mediated extraction. After polymer phase has been dissolved by very small amounts of an appropriate solvent, the concentrated polymer solution having low viscosity can directly be injected into a HPLC instrument, indicating that all analytes incorporated in extracting materials are introduced to the analytical instruments.

In conclusion, the results obtained in this study exhibit that polymer-mediated extraction methodology is quite effective for concentrating trace nonylphenol

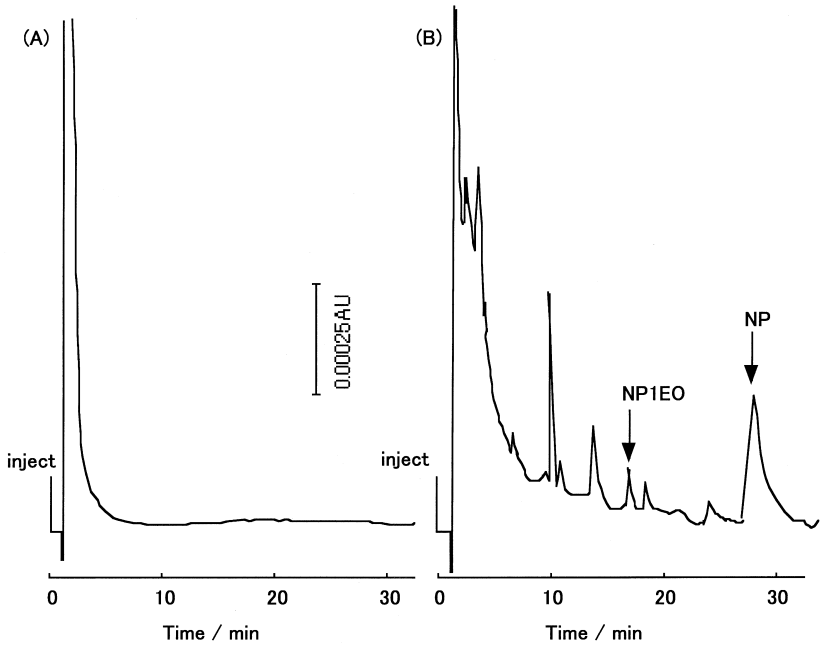

Fig. 3. Chromatograms of river water. (A) without concentration, (B) with polymer-mediated extraction. Column; Inertsil ODS ϕ4.6 mm×250 mm, mobile phase; 30% (v/v) aqueous acetonitrile, flow rate; 1.0 ml min^{-1}, detection wavelength; 254 nm.

and its polyethoxylate derivatives in water samples prior to a chromatographic analysis with a photometric detection. Good recovery of nonylphenol surfactants possessing a short polyethoxy chain is favorable for selective concentration of nonylphenols having high toxicity and persistence. The ability for concentrating not only hydrophobic compounds but amphiphiles would greatly extend the feasibility to apply polymer-mediated extraction to several analytes in a great variety of water samples.

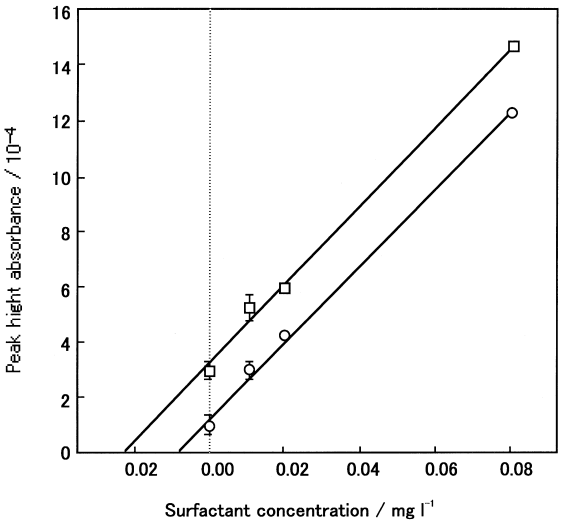

Fig. 4. Calibration curves for NP and NP1EO. (○) NP, (□) NP1EO. Error bar represents disperse of 5 runs. Point having no error bars is the average of triplicate runs.

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