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Cloud-point extraction of selected polycyclic aromatic hydrocarbons by nonionic surfactants

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Abstract

Effect of nonionic surfactants on the performance of the cloud-point extraction (CPE) processes in preconcentrating trace amount of polycyclic aromatic hydrocarbons (PAHs), consisting of two to five fused rings, from aqueous solution at 25 °C was studied. Three biodegradable nonionic surfactants with molecular similarity were employed. Cloud-point temperatures (CPTs) of these micellar solutions were regulated and reduced enough with addition of sodium sulfate and sodium phosphate, so that the CPE process could be facilitated at 25 °C. Furthermore, quadratic equations in additive concentration are found to fit the CPTs of these micellar solutions well. It is observed that the preconcentration factor could be enhanced either by increasing the salt concentration or by decreasing the initial surfactant concentration present in the micellar solution. With CPTs regulated at around 15 and 18 °C with addition of Na_2SO_4 and Na_3PO_4, preconcentration factors in between 30 and 45 obtained from 1 wt% micellar solutions of these three surfactants appear in the order of Tergitol 15-S-9 > Neodol 25-7 > Tergitol 15-S-7, coincidently with the hydrophilicity order of surfactants. The average preconcentration factor was empirically fitted well as a simple power-law function of surfactant concentration used in the CPE process. The obtained empirical power-law indices are close to negative unity.

Keywords: Cloud-point extraction (CPE); Preconcentration; Nonionic surfactants; Polycyclic aromatic hydrocarbon (PAH); HPLC analysis

1. Introduction

Surfactant-based extraction methods to preconcentrate trace solutes of grave environmental concerns from aqueous solutions have become more and more attractive [1–17], as water is often utilized as the main solvent in such methods, in contrast to the massive use of volatile organics in the conventional liquid–liquid extraction techniques [18–20]. Among these surfactant-based extraction techniques, the one based on the clouding phenomenon of surfactants, called the cloud-point extraction (CPE) method, is the most popular [4–16]. In general, a CPE process usually brings in a preconcentration factor about a few tens.

The cloud-point temperature (CPT), or equivalently the lower critical consolute temperature, is the specific temperature at which the clear micellar solution of a weekly polar surfactant, such as nonionic or zwitterionic surfactant, becomes turbid upon heating or cooling [21–24]. Explicitly for nonionic surfactants, at temperatures above the cloud point, the homogeneous surfactant solution separates into two immiscible phases with well defined composition, one of which contains much of surfactant, called surfactant-rich phase or coacervate phase, whereas the other, called water phase, is almost free of micelles and has a surfactant concentration near its critical micelle concentration (CMC) [21–24]. In general, nonionic surfactants are utilized in most CPE processes.

Moreover, the phase volume of the surfactant-rich phase is usually relatively small compared to that of the bulk phase. Namely, above the cloud point, the hydrophobic components initially present in the solution and bound to the micelles will be favorably extracted to the surfactant-rich phase, while leaves only a very small portion in the water phase. Consequently, solutes are preconcentrated in the surfactant-rich phase, which is also known as the CPE process [4–16].

The CPE technique was firstly introduced by Watanabe and Tanaka to preconcentrate metal ions from aqueous samples [9]. Subsequently, the scope of CPE technique was extended to

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extraction of proteins, enzymes and other biological products [10,11]. Moreover, it has been successfully demonstrated in the extractions of environmental organic pollutants for further chemical analysis as well [4,11–16].

As a new separation technique, the CPE has also shown itself as a promising preconcentration technique, which could provide good compatibility with hydroorganic mobile phase in the sample analysis using HPLC [11–16]. However, the performance of a CPE process is influenced by many factors, such as the cloud-point temperatures and concentrations of surfactants used, operational temperature of extraction process, physicochemical properties of solutes themselves, etc. [8,11,12]. Explicitly, surfactant plays a pivotal role in a CPE process. Therefore, proper choice of surfactant could lead to satisfactory performance of a CPE process.

The typical surfactants used in the CPE processes include Triton series, Igepal series and PONPE series (polyethyleneglycol mono-4-nonylphenyl ethers), etc. [6–10]. Unfortunately, these surfactants contain alkyl phenyl groups in their hydrophobic moiety, leading to some environmental concerns [25,26]. To alleviate this problem, biodegradable surfactants, mainly ethoxylated alcohols without phenyl group and branched alkyl chains, are proposed [4,12,15–17]. However, in the open literature, little emphasis has been addressed on the effect of molecular structures of these surfactants to the performance of a CPE process. Therefore, it is one of our aims to investigate this problem in this work. Moreover, extraction efficiency as a function of different molecular structure of surfactants is studied.

Three biodegradable nonionic surfactants with molecular similarity, Tergitol 15-S-7, Tergitol 15-S-9 and Neodol 25-7, were chosen in this work along with nine hydrophobic polycyclic aromatic hydrocarbons (PAHs), having two to five fused rings, as model extracts. PAHs give rise to great environmental concerns because they are either known or suspected carcinogens and mutagens even at trace level [27,28]. Their aqueous solubilities are low, because of their high hydrophobicity. Accordingly, strict legal controls are now imposed to regulate their production, usage and emission, in which the determination of trace of PAHs has to be addressed. Consequently, preconcentration treatment of such samples prior to analyses may be warranted [3,12,14].

Tergitol 15-S-X (X = 7 or 9) surfactants are polyethoxylated secondary alcohols, whereas Neodol 25-7 is a primary one. Tergitol 15-S-7 and Neodol 25-7 have close molecular weight and the same average number of ethylene oxide (EO) units. Likewise, Tergitol 15-S-7 and Tergitol 15-S-9 only differ in the chain length of their hydrophilic moieties, i.e. the EO number.

The CPE process could take place only at any temperature higher than the CPTs of the nonionic micellar solutions. To facilitate the CPE process, very often, heating is necessarily called up. The other alternative is to add in proper additives to suppress the CPTs of these micellar solutions low enough below the process temperature. In this work, effects of electrolytic additives were studied priorly, from which sodium sulfate and sodium phosphate were found to effectively serve this function. Amounts of additives are deliberately regulated, so that the CPTs of surfactant solutions fall in a narrow range, *circa* within 2 °C, for each series of experiments. Extraction efficiency and performance of the CPE processes are compared in order to shed a light on the understandings in the effect of molecular structures of surfactants to the CPE.

To our knowledge, it is the first time in the open literature that, with approximately the same cloud-point temperatures, higher preconcentration factors are resulted from the micellar solutions of surfactants with higher hydrophilicity, as shown in this work. For example, with CPT adjusted to ca. 15.5 °C by introducing proper amount of Na_2SO_4 to 1 wt% surfactant micellar solutions, Tergitol 15-S-9 happens to have the largest preconcentration factor in average at 40.5 ± 2.0, followed by 36.4 ± 0.94 of Neodol 25-7 and 28.0 ± 2.2 of Tergitol 15-S-7, which is coincident with hydrophilicity order of surfactants. This intriguing outcome certainly provides one criterion for choosing proper surfactants for a CPE process. Furthermore, more experimental findings and discussions are presented in this report.

2. Materials and methods

2.1. Materials

Three readily biodegradable nonionic surfactants were used in this work. They are Tergitol 15-S-5 and Tergitol 15-S-9, both acquired from Union Carbide (Danbury CT), and Neodol 25-7 (Ethylene Glycols Singapore Pte. Ltd., Singapore). Nonionic surfactants, Tergitol 15-S-7 and Tergitol 15-S-9 are mixtures of secondary alcohol ethoxylates with the alcohol group located at various positions along a chain of 11–15 carbon atoms and with an average EO number of 7.3 and 8.9, respectively. Neodol 25-7 is a mixture of linear primary alcohol ethoxylates with the alcohol group located at various positions along a chain of 12–15 carbon atoms and with an average ethylene oxide number of 7.3. Their selected properties were tabulated in Table 1.

Analytical grade of polycyclic aromatic hydrocarbons (PAHs) were purchased from Fluka and Aldrich. These PAHs include naphthalene (Nph), acenaphthene (Acp), fluorine (Flr), anthracene (Ant), phenanthrene (Pnt), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (Baa), benzo[a]pyrene (Bap) and perylene (Pel). Table 2 lists their selected physicochemical properties. Reagent grade of sodium sulfate and sodium phosphate, and HPLC-grade of acetonitrile were purchased from Fluka and

Table 1
Selected properties of nonionic surfactants

Surfactant	Molecular structure	Molecular weight (g/mol)	HLB	CMC (mg/L)	Cloud point[a] (°C)
Tergitol 15-S-7	$C_{11–15}H_{23–31}O(CH_2CH_2O)_{7.3}H$	515	12.4	39	38.0
Neodol 25-7	$C_{12–15}H_{23–31}O(CH_2CH_2O)_{7.3}H$	524	12.3	9	46.2
Tergitol 15-S-9	$C_{11–15}H_{23–31}O(CH_2CH_2O)_{8.9}H$	584	13.3	56	62.0

[a] Measured in 1 wt% surfactant solution.