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A new generation of nano-structured supramolecular solvents based on propanol/gemini surfactant for liquid phase microextraction

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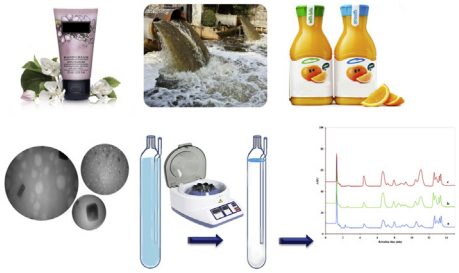
HIGHLIGHTS

- A supramolecular solvent (SUPRAS) made up of aggregates of gemini surfactant was introduced.
- A microextraction method, based on the SUPRAS was applied for extraction of parabens.
- Separation and determination of the parabens was performed by HPLC-UV.
- Parameters affecting extraction of the analytes were optimized by one variable at a time method.
- Under the optimal conditions, the preconcentration factors in the range of 98–156 were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

A new supramolecular solvent (SUPRAS) made up of aggregates of gemini surfactant was introduced. A microextraction method, based on the SUPRAS followed with high performance liquid chromatography-ultraviolet detection, was applied for the determination of parabens in cosmetics, beverages and water samples. A SUPRAS is a nano-structured liquid made up of surfactant aggregates synthesized through a self-assembly process. In the present work, a new gemini-based SUPRAS was introduced. Methyl paraben (MP), ethyl paraben (EP), and propyl paraben (PP) were extracted on the basis of π–cation and Van der Waals interactions into the SUPRAS. The parameter affecting the extraction of target analytes (i.e., the amount of surfactant and volume of propanol as major components comprising the supramolecular solvent, sample solution pH, salt addition, ultrasonic and centrifugation time) were investigated and optimized by one-variable-at-a-time method. Under the optimum conditions, the preconcentration factors of 98, 143 and 156 were obtained for MP, EP and PP, respectively. The linearity ranged from 0.5 to 0.7–200 μg L^{-1} with the correlation of determination of (R^2) ≥ 0.9938. The gemini-based SUPRAS followed by HPLC-UV has been found to have excellent detection sensitivity with a limit of detection (LOD, S/N = 3) of 0.5 μg L^{-1} for EP and PP, and 0.7 μg L^{-1} for MP. Good recoveries over the range of 92.0–108.3% assured the accuracy of the amount of parabens distinguished in the non-spiked samples.

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1. Introduction

Parabens (synthetic alkyl esters of *p*-hydroxybenzoic acid), which have been widely used in food, health care and especially cosmetic products as antifungal and preservative agents, have been designated as emerging contaminants [1]. Their advantages, including an extensive spectrum of activity, low cost, and their chemical and thermal stability over a wide pH range, make them highly attractive [2]. But it has been found that, in addition to disrupting the endocrine human system, the encouragement of female breast cancer is the consequence of fast absorption of parabens through dermal contact [3,4]. This serious condition has led to the restriction of the application of these compounds by regulations of national organizations [5]. The Council Directive 76/768/EC of the European Community permits their use with a maximum concentration of 0.4% (w/w) for each one and total maximum concentration of 0.8% (w/w).

The determination of parabens has been mainly based on high performance liquid chromatography (HPLC) with ultraviolet (UV) detection accompanied with different extraction methods, including dispersive liquid-liquid microextraction (DLLME) [6], hollow fiber liquid phase microextraction (HF-LPME) [7], solid phase extraction (SPE) [8], solid-phase microextraction (SPME) [9], stir-bar sorptive extraction (SBSE) [10], solidified floating vesicular-coacervative drop microextraction (SFVCDME) [11], and magnetic solid-phase extraction (MSPE).

In order to clean up and concentrate an analyte in different complex matrixes, sample preparation is inevitable [12]. Liquid-liquid extraction (LLE) has undoubtedly been an efficient tool in sample preparation [13]. Nevertheless, its disadvantages including large consumption of an organic solvent and sample solution has caused its replacement by other alternative microextraction techniques, such as single drop microextraction (SDME) [14], (HF-LPME) [13], and DLLME [15]. Microextraction methods are very important because of their versatility, simplicity, ease of operation, and high speed.

Recently, a novel type of synthetic surfactants, called gemini surfactants, has been created from the covalent linking of two ordinary surfactants via a spacer. These surfactants represent a series of superior properties in comparison with conventional single-chain surfactants. The dicationic quaternary ammonium compounds referred to as $C_MC_SC_M$ (Me), where M and S stand for the number of carbon atoms in the side alkyl chain and the methylene spacer, have been by far the most investigated dimeric surfactant. These are the most widely-studied gemini surfactants that are designated as m-s-m (Me). These surfactants are about three orders of magnitude more effective at lowering down surface tension and two orders of magnitude more efficient at forming micelles than are conventional ionic surfactants. These astonishing properties were ascribed to the distortion of water structure by the two hydrophobic tails in the molecule [16,17].

Supramolecular solvents (SUPRASs) were first introduced by Pérez-Bendito et al. in 2007 [18]. Recent term introduced to design nano-structured water-immiscible liquids generated from supramolecular assemblies of amphiphiles, which occurred on two scales: molecular and nano. It has been demonstrated that any solute establishing electrostatic or hydrophobic interactions (or both) with the micellar aggregations can be extracted to the surfactant rich phase (SUPRAS). SUPRASs have drawn increasing attention owing to their two important properties: changing solvent properties by varying the hydrophobic or polar group of the amphiphiles; and the presence of different polarity regions in the supramolecular aggregates that provide excellent extracting properties owning to a variety of interactions with analytes [19]. Until now, the extraction properties of tetrabutylammonium-induced coacervation in the vesicular solution of alkyl carboxylic acid [20], water-induced coacervation of alkyl carboxylic acid reverse micelles [18] and environmental responsive alkanol-based SUPRASs have been investigated [21].

Recently, our group reported a new method called gemini-based SUPRAS and investigated its ability to extract and preconcentre two pyrethroids from water and soil samples. The extraction is accomplished by migration of analytes to the supramolecular assemblies, composed of 14-2-14 gemini surfactant dissolved in tetrahydrofuran (THF). Due to approximately low solubility of gemini surfactant in THF, optimization faced some problems such as lack of reproducibility, narrow surfactant amount and THF volume range in which SUPRAS forms. To deal with these limitations, this research was intended to use propanol as a magic solvent for gemini based-SUPRASs. The Krafft temperature (T_k) is a point of phase change below which the surfactant stays insoluble in an aqueous solution. In fact, T_k is the minimum temperature at which surfactants form micelles. Increasing the alkyl chain carbon number (m) leads to an increase in T_k. All long alkyl chain m-s-m surfactants ($m \geq 14$) with a shorter spacer than 8 have such a high T_k that result in the precipitation of the solid surfactant at room temperature [23]. By taking account of these reasons, 14-2-14 (Me) is rarely soluble in water so that it can be considered insoluble whereas it dissolves well in 1-PrOH as a green solvent. The development of SUPRASs through the introduction of gemini-based SUPRAS has extended the scope of these solvents with regard to the numerous polarity regions of analytes that can be extracted, which derived from the special structure of gemini surfactants. All parameters that could influence the extraction efficiency of parabens were precisely studied. The gemini-based SUPRAS followed by HPLC-UV has been found to have good limit of detection (LOD, S/N = 3) of 0.5 μg L^{-1} for EP and PP, and 0.7 μg L^{-1} for MP. Also good recoveries over the range of 92.0–108.3% assured the accuracy of the amount of parabens distinguished in the non-spiked samples.

2. Experimental

2.1. Chemicals and reagents

Analytical grade MP, EP and PP were purchased from Sigma (St. Louis, MO, USA). *N,N,N′,N′*-tetramethyl-ethylenediamine (TEMED), bromotetradecane, acetone (Ace), hexane (HEX), diethyl ether, ethanol (EtOH), propanol (1-PrOH), sodium chloride (NaCl), nitric acid (HNO_3) and sodium hydroxide (NaOH) were purchased from Merck (Darmstadt, Germany). HPLC grade methanol (MeOH) and acetonitrile (ACN) were supplied by Duksan (Ansan, Korea). A model Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea) was used to prepare the ultra-pure water. The individual stock standard solutions of each paraben (1000 mg L^{-1}) were prepared in MeOH and stored at 4 °C. Different working solutions were prepared by appropriate dilution of stock solutions in MeOH. A concentration of 100 μg L^{-1} for each paraben was used for the subsequent experiments.

2.2. Apparatus

Nuclear magnetic resonance (^{1}H NMR 500 MHz) spectra were acquired by a Bruker DRX-500 AVANCE spectrometer and using DMSO as the solvent. Chemical shifts were reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) were reported in hertz (Hz), and spin multiplicities were indicated by the following symbols: s (singlet), d (doublet), t (triplet) and m (multiplet). A Thermo Scientific