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A novel preconcentration strategy for extraction methods based on common cationic surfactants: An alternative to classical coacervative extraction

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ABSTRACT

A novel and simple preconcentration step for aqueous micellar solutions of the common cationic surfactant cetyltrimethylammonium bromide (CTAB) has been developed. The procedure is based on the formation of another phase (a micro-droplet), not soluble in water, in which analytes (originally present in the aqueous solution) experience preconcentration. The method resembles to that of classical coacervation, but it does not require high ionic strengths neither acidic pH values. The optimum method implies mixing aqueous micellar solutions of CTAB with lithium bis[(trifluoromethane)sulfonyl]imide (Li-NTf_2) in a 1:1 molar ratio with a 16.5% (v/v) of acetonitrile content, followed by vortex, heating at 65 °C during 2 min, and centrifugation. The obtained microdroplet containing analytes is then subjected to high-performance liquid chromatography (HPLC) with diode-array detection (DAD). The method has been applied to the determination of a group of organic contaminants including alkylphenols, polycyclic aromatic hydrocarbons and parabens, present in aqueous samples (including seawater) or solid samples (such as sediment samples, which are subjected to a previous microwave-assisted extraction). Average preconcentration factors of roughly 14 and 12 are obtained for aqueous and sediment samples, respectively; being the limits of quantification down to 0.5 $\mu g\,L^{-1}$ and 0.02 $mg\,kg^{-1}$, respectively.

1. Introduction

Surfactants have been widely used in analytical chemistry as extractant solvents, with the purpose of replacing conventional organic solvents in extraction methods [1–4]. Among cationic surfactants, cetyltrimethylammonium bromide (CTAB) undoubtedly constitutes a paradigmatic example that self-assembles as micelles, and other structures and phases, depending on its concentration and solvent characteristics. CTAB has been widely employed in analytical chemistry with different purposes [5–10].

Contrary to the common analytical preconcentration approach for non-ionic and zwitterionic surfactants (the cloud-point extraction, CPE) upon heating, cationic surfactants do not suffer phase separation unless extreme pH values [11] or high ionic strengths [12] are used. Strong bindings of counterions have been postulated as a necessary condition for phase separation of ionic surfactants [13,14]. Hence, it is much better to use the term CPE when referring to the phase separation of neutral surfactants induced by temperature, whereas the term coacervative extraction (CAE) must be used for the phase separation of ionic amphiphiles induced by other conditions [1,15].

The classical CAE is hardly used for cationic surfactants with analytical purposes, due to the extreme conditions required. As an example, Jin et al. have used alkyltrimethylammonium micelle-based coacervates to extract chlorophenols efficiently, but the method requires a high NaCl content (400 $g\,L^{-1}$) [12].

Pérez-Bendito et al. have efficiently used ionic supramolecular assembly-based coacervates with analytical purposes, rather than solely cationic surfactants [16–19].

Several authors have proposed different approaches shifted to develop preconcentration steps for cationic surfactants. Many of them are based on mixing a cationic surfactant with a non-ionic surfactant to perform a phase separation phenomena with the mixed micelle under mild conditions of pH or ionic strength [20–22]. The combined use of cationic and nonionic surfactants also facilitates an increase in the extraction efficiency of polar organic compounds.

Ionic liquid-based surfactants, which can be classified as cationic surfactants, have been recently proposed as an attractive alternative in extraction methods [23–26] and in other fields within separation science [27]. A novel preconcentration procedure has been proposed for them, based on the formation of a micro-droplet of a non-water soluble IL-based surfactant *via* a simple metathesis reaction [28,29]. Thus, the first application involved

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the transformation of a water soluble IL-based surfactant (specifically 1-hexadecyl-3-butylimidazolium bromide, $C_{16}C_4$Im-Br) into a water insoluble IL (specifically 1-hexadecyl-3-butylimidazolium bis[(trifluoromethane)sulfonyl]imide, $C_{16}C_4$Im-NTf_2) [28]. Such metathesis reaction was successfully accomplished by adding the lithium salt Li-NTf_2 while ensuring a mol:mol ratio between $C_{16}C_4$Im-Br and Li-NTf_2. The Li-NTf_2 salt has been frequently proposed in IL-based preconcentration strategies intended for organic compounds [28,29], whereas the hexafluorophosphate sodium salt (Na-PF_6) is normally the choice when the preconcentration of metals is intended [30]. After the application of vortex and centrifugation, it takes place the formation of a micro-droplet of $C_{16}C_4$Im-NTf_2. The method was optimized to achieve a small micro-droplet of $C_{16}C_4$Im-NTf_2 compared to the initial volume of $C_{16}C_4$Im-Br aqueous solution, and so to ensure a high preconcentration for analytes originally present in the aqueous solution of $C_{16}C_4$Im-Br. A similar approach has also been recently proposed for the IL-based surfactant 1-hexadecyl-3-methylimidazolium bromide (C_{16}MIm-Br) [29] using Li-NTf_2, but in this case it is necessary to add acetonitrile and to heat the solution before vortex and centrifugation. The IL nature is clearly exerting a noticeable influence in the performance of the preconcentration step. Indeed, the substitution of a butyl- for a methyl-substituent in the IL-based surfactant has implied an important modification in the conditions needed to observe a phase separation phenomena.

The main purpose of this work is to evaluate if such preconcentration approach, valid for IL-based surfactants, it is also adequate for the common cationic surfactant CTAB. This preconcentration step could constitute an alternative to the extreme conditions normally required in classical CAE for cationic surfactants. Furthermore, analytical applications of CTAB can be expanded due to an increase in the overall sensitivity of extraction methods involving this (or another) cationic surfactant. The preconcentration method for CTAB has been developed for a group of organic contaminants, including alkylphenols and polycyclic aromatic hydrocarbons, present in aqueous samples and in sediments.

2. Experimental

2.1. Reagents and materials

The cationic surfactant cetyl-trimethyl-ammonium bromide (CTAB, $C_{16}M_3$N-Br) was supplied by Aldrich (Beerse, Belgium). The salt lithium bis[(trifluoromethane)sulfonyl]imide (Li-NTf_2) was supplied by Sigma–Aldrich GmBH (Steinheim, Germany).

Artificial seawater was prepared by dissolving the following salts in 1 L of deionized water: Na_2SO_4 (4.00 g), KCl (0.70 g), $MgCl_2 \cdot 6H_2O$ (10.78 g), $NaHCO_3$ (0.20 g) and NaCl (23.50 g).

The polycyclic aromatic hydrocarbons (PAHs) studied were benzo(a)anthracene (BaA) and benzo(a)pyrene (BaP), both supplied by Aldrich, and benzo(k)fluoranthene (BkF), supplied by Sigma–Aldrich Chemie GmBH (Steinheim, Germany). Individual standard solutions of these analytes were prepared in acetonitrile with concentrations ranging from 950 to 990 mg L^{-1}.

The alkylphenols used in this study were 4-*tert*-butylphenol (*t*-BP), 4-octylphenol (OP), 4-cumylphenol (4-CP), 4-*n*-nonylphenol (NP), and bisphenol-A (BPA). They were all supplied by Sigma–Aldrich Chemie GmBH, except NP, which was supplied by Alfa-Aesar (Karlsruhe, Germany). Individual standard solutions of these analytes were prepared in acetonitrile with concentrations ranging from 910 to 1170 mg L^{-1}.

The paraben used in this study was butylparaben (BuP) supplied by Sigma–Aldrich Chemie GmBH. Individual standard solution of this paraben was prepared in acetonitrile at 970 mg L^{-1}.

Standard solution mixtures containing paraben, alkylphenols and PAHs were prepared at concentration values ranging from 10 to 60 mg L^{-1} in acetonitrile for the focused-microwave-assisted extraction procedure.

Standard solution mixtures containing paraben, alkylphenols and PAHs were prepared at concentration values ranging from 0.2 to 1.2 mg L^{-1} in acetonitrile for the preconcentration procedure.

Acetonitrile of HPLC grade (Merck, Darmstadt, Germany) was used for all dilutions. Deionized water was obtained from a Milli-Q gradient A10 system (Millipore, Bedford, MA, USA). All the solvents were filtered through a 0.45 μm Durapore® membrane filter (Millipore) before being used in the chromatographic system.

KIMAX® centrifuge tubes (Sigma–Aldrich), with 35 mL of capacity, were used in the microwave. Stir bars of 10 mm × 3 mm were also obtained from Sigma–Aldrich. PIREX® centrifuge tubes with 20 mL of capacity were used for the preconcentration procedure.

The method was validated using the certified reference material CRM-535, river harbor sediment, certified by BCR and revised under the responsibility of the Institute of Reference Materials and Measurements (IRMM, Geel, Belgium). This material was provided by LGC Promochem (Barcelona, Spain). This reference material is well-characterized, with an organic matter content of 12% (mass fraction), pore size < 2 mm, and certified for seven individual PAHs, 3 of them included in the present study.

One real marine sediment sample was collected from the coasts of Tenerife (Canary Islands), in an area known for its low levels of contamination. This sediment, with an organic matter content of 27.3 g kg^{-1}, was used as a blank. After sieving, fractions of sediment with particle size < 250 μm were taken and used for subsequent analysis.

2.2. Instrumentation

Focused microwave-assisted extractions were performed at atmospheric pressure using a CEM Focused Microwave™ Synthesis System apparatus, model Discover (CEM Corporation, Matthews, NC, USA) equipped with an infrared temperature control system, stirring and cooling options. The cooling is carried out by means of a flow of air.

A vortex model reax-control from Heidolph Instruments GMBH (Schwabach, Germany), and an Eppendorf Centrifuge model 5702 (Hamburg, Germany) were also used in the studies. The heating plate, model RCT Basic was supplied by IKA® Werke (Staufen, Germany).

The HPLC equipment consisted of a gradient system L-2130 Merck Hitachi Pump (supplied by Merck) and a Rheodyne valve (Supelco, Bellefonte, PA, USA) with a 20 μL loop. The detection was carried out using a diode array detector (DAD) ProStar 330 supplied by Varian (Palo Alto, CA, USA). Data acquisition was carried out with the Star 5.51 software by Varian. The analytical column was a C18 Res Elut HPLC Column (5 μm, 150 mm × 4.6 mm) supplied by Varian, and protected by a Pelliguard LC-18 guard column (Supelco). The syringe used for HPLC injection was a Hamilton (Reno, NV, USA) of 100 μL.

2.3. Procedures

2.3.1. Preconcentration procedure

During the optimization study of the preconcentration procedure, different aliquots of CTAB solutions in deionized water, in artificial seawater, or in the sediment extract (in this last case with a fixed CTAB concentration of 40 mM), were mixed with different aliquots of aqueous solutions of Li-NTf_2 0.5 g mL^{-1}. The 1:1 molar ratio between CTAB and the added Li-NTf_2 was always kept. These mixtures were then mixed with acetonitrile, vortexed, heated, and centrifuged. The specific volume of the micro-droplet