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Evaluating solid phase (micro-) extraction tools to analyze freely ionizable and permanently charged cationic surfactants

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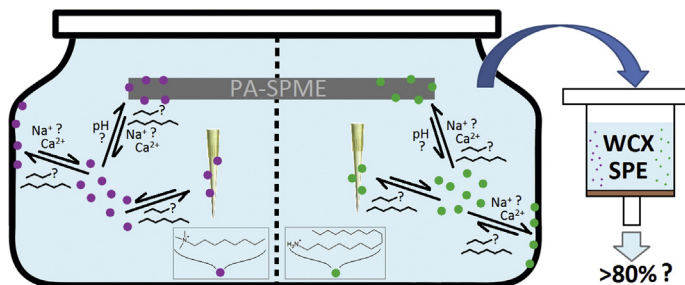
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HIGHLIGHTS

- An SPE method to measure 32 amine based cationic surfactants is proposed.
- Sorption of cationic surfactants to pipette tips and glassware is quantified.
- Charged compounds adsorb to and neutral compounds absorb into PA-SPME fibers.
- pH-dependency of sorption of cationic surfactants to PA-SPME fibers is explored.
- PA-SPME shows pH-dependency even for quaternary ammonium surfactants.

GRAPHICAL ABSTRACT



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ABSTRACT

Working with and analysis of cationic surfactants can be problematic since aqueous concentrations are difficult to control, both when taking environmental aqueous samples as well as performing laboratory work with spiked concentrations. For a selection of 32 amine based cationic surfactants (including C8- to C18-alkylamines, C14-dialkyldimethylammonium, C8-tetraalkylammonium, benzalkonium and pyridinium compounds), the extraction from aqueous samples was studied in detail. Aqueous concentrations were determined using solid phase extraction (SPE; 3 mL/60 mg Oasis WCX-SPE cartridges) with recoveries of $\geq 80\%$ for 30 compounds, and $\geq 90\%$ for 16 compounds. Sorption to glassware was evaluated in 120 mL flasks, 40 mL vials and 1.5 mL autosampler vials, using 15 mM NaCl, where the glass binding of simple primary amines and quaternary ammonium compounds increased with alkyl chain length. Sorption to the outside of pipette tips ($\leq 20\%$ of total amount in solution) when sampling aqueous solutions may interfere with accurate measurements. Polyacrylate solid phase microextraction (PA-SPME) fibers with two coating thicknesses (7 and 35 μm) were tested as potential extraction devices. The uptake kinetics, pH-dependence and influence of ionic strength on sorption to PA fibers were studied. Changing medium from 100 mM Na^+ to 10 mM Ca^{2+} decreases K_{fw} with one order of magnitude. Results indicate that for PA-SPME neutral amines are absorbed rather than adsorbed, although the exact sorption mechanism remains to be elucidated. Further research remains necessary to establish a definitive applicability domain for PA-SPME. However, results indicate that alkyl chain lengths ≥ 14 carbon atoms and multiple alkyl chains become problematic. A calibration curve should always be measured together with the samples. In conclusion, it seems that for amine based surfactants PA-SPME does not provide the

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reliability and reproducibility necessary for precise sorption experiments, specifically for alkyl chain lengths beyond 12 carbon atoms.

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1. Introduction

Cationic surfactants are commercially important compounds with diverse applications in industrial and household preparations such as detergents, preservatives, antiseptics, fabric softeners, and personal care products [1,2]. The combination of a positively charged head group and one or more hydrophobic alkyl chains gives cationic surfactants their amphiphilic properties. It is well known that these cationic surfactants have a strong sorption affinity to different kinds of surfaces [3], and they are acknowledged as emerging contaminants in sewage sludge and sediments [4]. In environmental risk assessment, sorption is an important parameter that has an effect on the distribution of a compound among different compartments in the environment, including the aqueous phase, soil, sediment and biota. Within the aqueous phase itself, sorption to dissolved organic matter may affect the bioavailability, bioaccumulation and effects on biota [5]. Particularly for strongly sorbing cationic surfactants, bioavailability is an important feature in risk assessment [3,6].

Within the context of bioavailability, the concept is that only freely dissolved molecules can cross biomembranes, and only the freely dissolved external concentration (C_{free}) will equilibrate with the internal tissue concentrations to exert (adverse) effects [7–9]. Solid-phase microextraction (SPME) is broadly used to measure the C_{free} of polar and non-polar analytes in a range of different matrices [10–13]. More recently, polyacrylate (PA) SPME has also been applied to sample quaternary ammonium based cationic surfactants [14,15]. PA-coated SPME fibers have sufficient cation exchange capacity (CEC) to effectively adsorb several nitrogen-based cationic surfactants to the fiber surface, whereas the CEC is low enough to prevent depletive extraction in most samples [5,15]. PA-SPME has specific benefits when dealing with environmental samples: (i) the SPME coating is in direct equilibrium with C_{free} , (ii) the small fiber volume (extraction phase) leads to selective isolation of analytes, resulting in relatively clean samples which can be analyzed without matrix effects, (iii) pH-modification of samples is not required for quantitative purposes since PA-SPME has sufficient affinity for positively charged species and can be calibrated at the required sample pH, (iv) the fiber structure eliminates problems related to typical sample clean-up steps using SPE or filter cartridges, such as solid phase clogging with suspensions and breakthrough volume with voluminous samples [16]. Thin film SPME (TFME) is a relatively new technique that has also been applied to sample cationic surfactants [17]. A detailed optimization of the TFME procedure was presented, including the evaluation of matrix effects [17]. TFME is mostly a depletive extraction technique, while for some situations non-depletive sampling might be preferable. Liquid-phase microextraction (LPME) has also been suggested for analysis of cationic surfactants, but preparation of LPME is more time consuming and the applicability is less versatile [18]. PA-SPME opens the possibility of non-depletive sampling and can also be applied offline, for instance during toxicity testing or when sampling multiple phases in a closed system (anaerobic sediment, aerobic sediment, supernatant). However, the sorption coefficient to the PA-SPME fiber has to be carefully calibrated for each cationic surfactant in every medium of interest.

The main aim of this manuscript was to elucidate the challenges

and limitations when using PA-SPME to sample the C_{free} of a wide range of cationic surfactants, thereby determining the boundaries of the applicability domain. Cationic surfactants were selected based on structural diversity and environmental relevance. Whereas previous studies with PA-SPME were limited to permanently charged quaternary ammonium compounds (QACs), the current study also included primary, secondary and tertiary amines, as well as several other types of QACs. Ionizable amines were included specifically as they exist partly as ionized and neutral species, depending on the pH, which may affect their affinity for PA-SPME [14,19].

It is well known that working with – and analysis of – cationic surfactants can be problematic, in the sense that aqueous concentrations are difficult to control. Losses can be expected from accumulation on gas-liquid or liquid-solid interfaces, and adsorption to negatively charged surfaces such as glassware, dissolved organic matter, clay particles, and biomolecules [5,15]. Significant binding to glassware and other laboratory equipment can be expected [5], as well as sorption to PTFE lined septa and surfaces [20,21]. Furthermore, the efficiency of electrospray ionization frequently employed with MS/MS analyses can be influenced by surfactants in a concentration-dependent manner [22].

In order to more easily determine and confirm aqueous concentrations in SPME calibration studies and adsorptive studies with laboratory equipment, this study tested the performance of a weak cation exchange solid phase extraction (WCX-SPE) cartridge for a wide range of cationic surfactants. In addition, sorption losses to glass vials and pipette tips was studied to assess flaws in experimental procedures and to design special methods to sample cationic surfactants most adequately. Sorption to glass was measured with five primary alkylamines (chain length range C_{10-18}) and five quaternary alkyltrimethylammonium compounds (chain length range C_{10-18}). Sorption was expected to increase with increasing chain length [23], which makes working with the longest chain cationics extremely challenging. Therefore, one of the objectives was to identify the boundaries for application of SPE and PA-SPME with respect to longer alkyl chain isomers.

Combining findings regarding glass binding and SPE, the recovery of WCX-SPE was measured for all test chemicals. WCX-SPE was then used to measure aqueous concentrations when calibrating PA-SPME fibers in different matrices. Calibration under different conditions opens the possibility to determine fiber-water sorption affinity (K_{fw}) as a function of exposure time, analyte concentration, pH or ionic composition, and reproducibility of the PA-SPME batch applied. Measuring K_{fw} of structural homologues could also lead to better understanding of the contribution of molecular structure to K_{fw} for PA-SPME fibers. The conclusions presented could guide future studies on the use of PA-SPME in environmental and toxicological studies for (hydrophobic) cationic surfactants.

2. Materials and methods

2.1. Selection of chemicals

An overview of the 32 selected compounds is given in Table 1. In their simplest form, these amines contain one alkyl chain (primary amines “P10, P12, P14, P16, P18”), and in addition one (secondary

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