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Fluorous receptor-facilitated solid phase microextraction

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ABSTRACT

Solid phase microextraction (SPME) is a widely accepted solvent-free extraction technique that usually uses a polymer sorbent as the extraction phase. In this work, we have developed receptor-doped fluorous films for solid phase microextraction. The hydrophobic and lipophobic properties of the fluorous films in principle reduce the polymer–water distribution coefficients of solutes other than those that can form noncovalent interactions with the fluorous receptor. This strategy should improve extraction selectivity. We found that the addition of a fluorous carboxylic acid (Krytox 157 FSH) to a fluorous film (Teflon AF 2400) increased the polymer–water distribution coefficients of quinoline, a nitrogen heterocycle. We studied the effects of receptor concentration and solute concentration on the distribution coefficients based on 96-well vessel SPME. We then coated this receptor doped fluorous polymer on a stainless steel fiber for SPME. Compared to a commonly used SPME fiber made of polydimethylsiloxane (PDMS), it showed a preference for the nitrogen heterocyclic compound over a non-heterocyclic control, phenol. To our knowledge, this is the first reported receptor-doped fluorous SPME.

1. Introduction

Sample preparation is an essential step in the analysis process. Solvent-free extraction is considered to be a green analytical method as it prevents hazards to the environment and human health. Solid phase microextraction (SPME) is a widely accepted solvent-free extraction technique that usually uses a polymer sorbent as the extraction phase. Various configurations of SPME have been considered to date, including coated fibers and vessels [1].

The selection of sorbent polymer material is the most important step controlling the selectivity of the extraction [2]. One of the recent trends in SPME is to study new coatings with higher extraction efficiency and selectivity [3]. Recently developed coatings for selective extraction include molecularly imprinted polymers (MIP) [4–11], ionic liquids [12–16], metal complexes [17], and carbon nanotubes [18,19]. We showed some time ago that a molecular receptor for barbiturates embedded in the extraction phase enhances the selectivity of SPME for barbiturates that bind well to the receptor [20]. Such receptors are potentially very powerful tools for selective extractions by taking advantage of noncovalent bonding between a receptor and an analyte. However, while receptors can improve selectivity by augmenting the distribution coefficient of the selected analytes, the matrix in which the receptor resides plays a role as well. Ideally, the matrix would decrease the distribution coefficient for uninteresting analytes while the receptor increases the distribution coefficient of interesting analytes. This notion guided us to fluorous solvents and materials as potential matrices for SPME.

Fluorous solvents are the least polar practical solvents known [21]. Fluorous liquids are virtually immiscible with both aqueous and most organic phases. Due to their extreme nonpolar character, noncovalent associations including hydrogen bonding tend to be enhanced in fluorous media [22]. Molecular recognition has been combined with fluorous matrices to improve extraction selectivity by reducing the interfering species extracted. Palomo et al. reported that the fluorous solubility of fluorinated N,N′-dialkylureas could be enhanced by embedding perfluoroalkanoic acids in perfluorohexanes (FC-72) due to formation of hydrogen bonded complexes [23]. O'Neal and coworkers also reported that a carboxylic acid terminated poly-hexafluoropropylene oxide, Krytox 157 FSH (**1**), significantly enhances the extraction of pyridines from chloroform into FC-72 by forming a hydrogen bond between the pyridine ring and the carboxylic acid group [24].

Teflon AF 2400 (**2**) is a chemically inert and thermally stable amorphous fluorinated polymer. It is a copolymer of tetrafluoroethylene (13%) and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (87%) [25]. Homogeneous thin films of Teflon AF 2400 are easily prepared through solvent casting [26]. They are transparent through a wide UV-Vis and IR range [27], making them ideal

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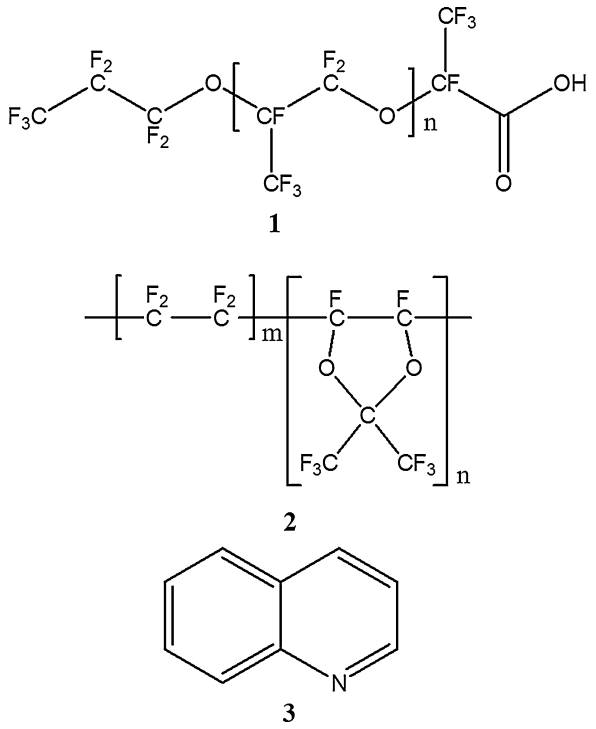

Fig. 1. Structure of Ktytox 157 FSH (**1**), Teflon AF 2400 (**2**), quinoline (**3**).

to study noncovalent associations. Teflon AF 2400 has a high fractional free volume (FFV) probably due to its rigid structure of the dioxolane ring and the weak van der Waals interactions between fluorous polymeric chains [28]. Krytox 157 FSH is thermally stable and can be easily incorporated into Teflon AF 2400 films. Krytox 157 FSH and Teflon AF 2400 were found to be miscible in any proportion [29]. We are interested in developing receptor-doped fluorous films for solid phase microextraction. The hydrophobic and lipophobic properties of the fluorous films will reduce the polymer–water distribution coefficient of all solutes except the ones that can form noncovalent interaction with the fluorous receptor, making extractions selective (Fig. 1).

We recently reported a 96-well parallel design to measure distribution coefficients of novel drug-like compounds between a plasticized polyvinyl chloride (PVC) film and an aqueous phase [30]. This parallel design is fast and only requires small amounts of sample. In this work, we have applied this parallel approach to create a 96-well vessel SPME to study distribution between receptor-doped fluorous polymer phase and an aqueous phase. Based on previous results on hydrogen bonding of pyridine and pyridine derivatives with carboxylic acids in the fluorous liquids [24], we chose to study the distribution behavior of quinoline (**3**), an environmental contaminant and a probable human carcinogen [31], between a fluorous polymer phase composed of Krytox 157FSH doped Teflon AF 2400 and an aqueous phase.

We found that the addition of a fluorous carboxylic acid to the film increased the polymer–water distribution coefficients of the nitrogen heterocycle. We studied the effects of receptor concentration and solute concentration on the distribution coefficients based 96-well vessel SPME. We then coated this receptor doped fluorous polymer on a stainless steel fiber for SPME. Compared to a commonly used SPME fiber made of polydimethylsiloxane (PDMS), Krytox 157-FSH doped Teflon AF 2400 showed a preference for the nitrogen heterocyclic compound over a non-heterocyclic control, phenol. To our knowledge, this is the first reported receptor-doped fluorous SPME.

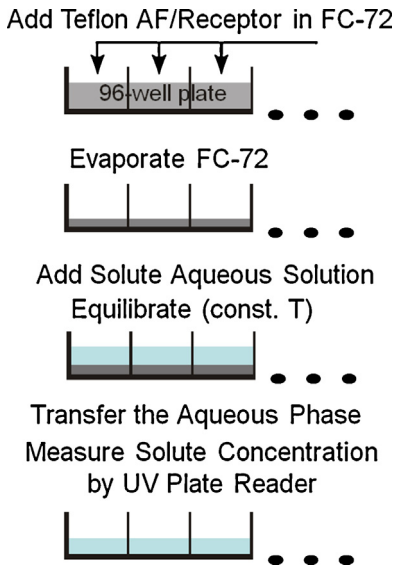

Fig. 2. General procedure for 96-well vessel SPME.

2. Experimental

2.1. Chemicals and solutions

Quinoline and tris (hydroxymethyl) aminomethane hydrochloride buffer substance (Tris buffer) were obtained from Aldrich (Milwaukee, WI). Phenol and nitric acid were bought from EM Science (Cherry Hill, NJ). Krytox 157FSH was purchased from Miller-Stephenson Chemical Co., Inc. (Danbury, CT) with a number averaged molecular weight of 5150 g/mol based on an average of 29 polymer repeat units determined by ^{19}F NMR [32]. Teflon® AF 2400 was purchased from DuPont (Wilmington, DE). Fluorinert FC-72 (a mixture of perfluorohexanes) was purchased from 3 M (St. Paul, MN). Aqueous tris(hydroxymethyl)aminomethane buffer (tris buffer hereafter) solutions (50.0 mM, pH = 8.0) were prepared by dissolving tris buffer pH 8.0 substance (Sigma Aldrich, Milwaukee, WI) in purified water (Milli-Q water) from a Millipore Synthesis A10 system (Millipore, Billerica, MA). Quinoline and phenol solutions with a variety of concentrations were prepared in this tris buffer.

2.2. 96-well vessel SPME: preparation and extraction

As outlined in Fig. 2, receptor-doped fluorous polymer films were prepared in Costar polypropylene 96-well microplates (flat-bottom, 330 μL well volume). Both Teflon AF 2400 and Krytox 157FSH were initially prepared in FC-72 at a concentration of 10 mg/mL. These solutions were combined to give 200 μL of a solution that would yield films with ratios of 0.0%. 12.5%, 25%, 37.5%, 50%, 75%, 100% (w/w) Krytox. Final film weights are therefore 2.0 mg. After the polymer films were formed, 200 μL aliquots of the aqueous solute-containing films solutions were added to undivided wells. Plates were sealed by a cover and equilibrated in a shaker (BioShaker MBR-022U, made by Taitec and distributed by Bionexux Inc., Oakland, CA) at 500 rpm at 25.0 °C. In order to determine the necessary equilibration time, the percentage of quinoline extracted into the polymer phase was measured as a function of time. Other than in this experiment, all data were generated at equilibrium. After equilibrium was achieved, 100 μL aliquots from each well were transferred into a UV-transparent microplate by a multichannel pipette. To determine the solute concentrations, UV absorbance was measured by a SpectraMax M2 microplate reader (Molecular