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Research paper

Detailed NMR investigation of cyclodextrin-perfluorinated surfactant interactions in aqueous media

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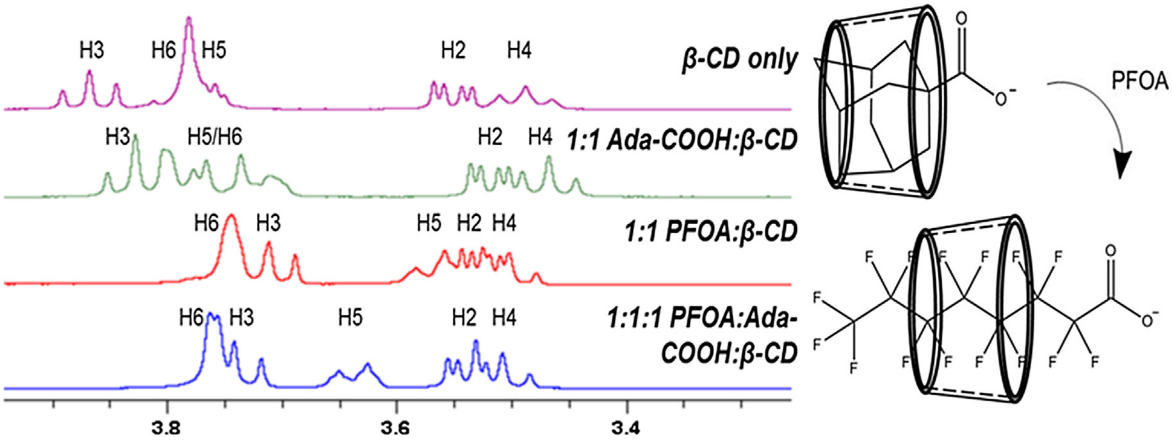
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Perfluorochemicals (PFCs) are strongly encapsulated by cyclodextrins (CDs).
- Competition studies confirm strong CD:PFC host-guest interactions.
- ^{19}F NMR Spectroscopy demonstrates association constants up to 10^5 M^{-1}.
- Position of CD along PFC chain is elucidated from NMR results.
- CD:PFC complex is not disturbed under a variety of water quality conditions.

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ABSTRACT

Perfluorochemicals (PFCs) are contaminants of serious concern because of their toxicological properties, widespread presence in drinking water sources, and incredible stability in the environment. To assess the potential application of α-, β-, and γ-cyclodextrins for PFC remediation, we investigated their complexation with linear fluorinated carboxylic acids, sulfonates, and a sulfonamide with carbon backbones ranging from C4-C9. ^{19}F Nuclear Magnetic Resonance (NMR) spectroscopy studies demonstrated β-CD formed the strongest complexes with these PFCs. The polar head group had a modest influence, but for PFCs with backbones longer than six carbons, strong association constants are observed for 1:1 ($K_{1:1} \sim 10^5$ M^{-1}) and 2:1 ($K_{2:1} \sim 10^3$ M^{-1}) β-CD:PFC complexes. Excess β-CD can be used to complex 99.5% of the longer chain PFCs. Competition studies with adamantane-carboxylic acid and phenol

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Remediation
NMR spectroscopy
Perfluorooctanoic acid

confirmed the nature and persistence of the β-CD:PFC complex. Detailed analyses of the individual NMR chemical shifts and Job plots indicate the favored positions of the β-CD along the PFC chain. Solution pH, ionic strength, and the presence of humic acid have modest influence on the β-CD:PFC complexes. The strong encapsulation of PFCs by β-CD under a variety of water quality conditions demonstrates the tremendous potential of CD-based materials for the environmental remediation of PFCs.

1. Introduction

Perfluorinated compounds (PFCs) are persistent organic pollutants and contaminants of emerging concern [1–5]. They encompass a unique class of molecules with a highly fluorinated carbon chain as the tail and a hydrophilic functional group as the polar head group, making them both lipophobic and hydrophobic [1,4]. The carbon-fluorine bonds are among the most stable single bonds known to organic chemists, lending these molecules extreme chemical and thermal stability. PFCs have been used as surfactants, emulsifiers, and surface coatings, with specific applications including aqueous film-forming foams (AFFFs) for oil fires and processing aids for fluoropolymer synthesis (such as PTFE and PVDF) [1]. PFCs are also by-products of fluoropolymer and fluorotelomer synthesis and have been detected in drinking water, consumer products, wildlife, and humans [1–8]. Exposure to ppb levels of PFCs have been linked to kidney, testicular, bladder, and liver cancer, thyroid disease, low birth weight, developmental delays, and infertility [4,8–13].

Typical drinking water treatment processes do not remove PFCs from the water supply, and in some cases can concentrate them [14,15]. Previous studies for PFC removal include adsorption using activated carbon; nanofiltration and reverse osmosis; and advanced oxidation processes and ultrasonic degradation [16–18]. In general these methods have marginal or limited levels of success, may require expensive equipment and/or long reaction or contact times, and may only transform longer chain PFCs to shorter chain, instead of eliminating the environmental threat [16].

Given their extreme resistance to chemical transformation, adsorption of PFCs appears to be a more promising strategy for their removal from water. With this in mind we herein report the study of cyclodextrins (CDs) as hosts to trap PFCs as a potential strategy for environmental remediation. Cyclodextrins, composed of simple glucose sugar residues, are inexpensive, abundant, renewable, water soluble, and non-toxic [19]. The three most common cyclodextrins are α-, β-, and γ-CD, composed of six, seven, and eight glucose monomers, respectively. CDs have been shown to remove various environmental pollutants such as PCBs, phenols, dyes, pharmaceuticals and heavy metals from aqueous media [19–24]. Cyclodextrins are toroid-shaped macrocyclic molecules with a hydrophilic exterior due to the alcohol functionalities and a hydrophobic interior lined with C—H bonds and the electron pairs from oxygen atoms. These characteristics make CDs attractive for host-guest chemistry-based applications [25–27]. A hydrophobic guest partitions favorably from the polar aqueous media into the cyclodextrin cavity. With their hydrophobic tail and hydrophilic head, PFCs can partition into the cyclodextrin cavity while the functional head group can be solvated by aqueous solution and interact with the hydroxyl groups on the cyclodextrin via hydrogen bonding [28,29].

Nuclear Magnetic Resonance (NMR) spectroscopy has been extensively exploited and is often the method of choice for investigating and determining the equilibrium association constants for host-guest complexes in solution [30–38]. The characteristic resonance frequency of an atom encapsulated within the CD molecule is expected to change with increasing host concentration due to shielding effects and dramatic differences in solvation [27,39]. Guo, et al. determined the equilibrium constants for 1:1 CD:PFC interactions [32], while Wilson and Verrall determined that 2:1 interactions also are present between β-cyclodextrin and perfluorocarboxylic acids [33,34]. More recent reports have further elucidated structural details of the host-guest interactions between β-CD and perfluorooctanoic acid (PFOA) in solution and solid state [36–38]. Remediation strategies of PFCs based on their strong CD complexation properties have begun to be explored, including molecularly imprinted polymers [40,41].

We herein report detailed studies of eight PFCs with different polar head groups and varying chain lengths. Careful NMR analyses provide detailed structural information of the β-CD:PFC complexes. Adamantane-carboxylic acid, a powerful β-CD inclusion guest, and phenol, a model environmental pollutant, were used to confirm the strength and nature of the β-CD:PFOA complex. The complex is robust under a variety of water quality conditions, including a range of ionic strength and solution pH values, and in the presence of humic acid. Our results demonstrate the promise of CD-based materials for the environmental remediation of a variety of fluorinated surfactants in a wide range of water quality conditions.

2. Experimental methods

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), hexafluorobenzene, adamantane-carboxylic acid, phenol, and humic acid were purchased from Sigma-Aldrich. Potassium perfluorooctane sulfonate (PFOS), perfluorooctanesulfonamide (PFOSA), and 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid (6:2 fluorotelomer sulfonate, 6:2 FTS) were purchased from SynQuest Labs. α-, β-, and γ-Cyclodextrin were purchased from Acros Organics. Deuterium oxide (99.9% D) was purchased from Sigma-Aldrich and stored at 4 °C. All chemicals were used without further purification. Structures and abbreviations can be found in the Supplementary Materials (S2-S3).

2.1. Sample preparation

Solutions of 2.42×10^{-3} M perfluorocarboyxlic acids and 6.05×10^{-4} M perfluorosulfonates/sulfonamide were prepared in 50% D_2O and 50% DI H_2O, adjusted with 0.036 M NaOH to solution pH 7. Hexafluorobenzene (0.17 μL, 1.44×10^{-3} M) was added as an internal standard. Various cyclodextrins were added in different stoichiometric ratios. Solutions were sonicated in a cleaning bath for five minutes to ensure dissolution of substrates.

2.2. Environmental conditions and competition studies

The competition studies were performed with PFOA, β-CD, and adamantane-carboxylic acid or phenol. The studies on the effects of environmental conditions on the complex were performed with PFOA and β-CD. For the ionic strength experiments, NaCl at 0.01,