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Separation and fluorine nuclear magnetic resonance spectroscopic (^{19}F NMR) analysis of individual branched isomers present in technical perfluorooctanesulfonic acid (PFOS)

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ABSTRACT

The production of perfluoroalkylsulfonate (PFOS) derivatives from linear alkyl precursors using electrochemical fluorination is not a clean process but, instead, gives complex mixtures. This study reports the isolation and ^{19}F NMR characterization of eleven perfluorooctanesulfonate isomers from a commercial mixture. This allowed the quantification of the individual CF_3 branched isomers that predominate in technical PFOS.

1. Introduction

The production of perfluoroalkylsulfonate (PFOS) derivatives from linear alkyl precursors using electrochemical fluorination is not a clean process but, instead, gives complex mixtures (3M Company, 1999, 2000). The presence of C_8 branched isomers in commercial perfluorooctanesulfonate (PFOS) is evidenced by their partial separation by liquid chromatography (LC), often resulting into two broad peaks (Takino et al., 2003; Kubwabo et al., 2004; Kuklenyik et al., 2004). In other LC studies, the isomers were reported to elute as a broad peak (Hansen et al., 2002; Moody et al., 2002).

Indeed, commercial PFOS is largely (about 90%; see Seacat et al., 2003), a mixture of *ca* 70% linear (**1a**) and *ca* 30% branched isomers (**2a**–**9a**) as measured by ^{19}F NMR spectroscopy (3M Company, 1997; Martin et al., 2004) (90% also includes small amounts of impurities including shorter chain homologues of PFOS, perfluoroalkanoic acids and partially fluorinated compounds). The ^{19}F NMR study (3M Company, 1997) allowed quantification, individually, of some of the major isomeric compounds present, namely, the normal chain (**1a**), F_7-isopropyl branched (**7a**), alpha branched (**2a**), F_9-*t*-butyl branched (**8a**) and internal *gem*-di-CF_3 branched (**9a**) isomers. Apparently however, it was not possible to quantify the CF_3 branched isomers **3a**, **4a**, **5a** and **6a**, presumably due to the similarity of their structures and of their ^{19}F NMR spectra and the fact that their concentrations in the technical mixture are low. To our knowledge, there are no reports of the isolation of individual isomers allowing unequivocal assignments of the resonances in their ^{19}F NMR spectra.

One current interest in being able to identify and quantify as many as possible of the individual branched isomers present in commercial PFOS arises from the possibility that they may exhibit differences in toxicity. Any differences found will be important for future risk assessment of PFOS. However, one study (Yoo et al., 2005) has indicated that the different PFOS isomers may have similar toxicity profiles, at least in one specific assay system (gap junction intercellular communication), but more work is necessary.

The objective of the present work was to isolate the main perfluorooctanesulfonate isomers present in a mixture prepared from technical perfluorooctanesulfonyl fluoride (PFOSF) and to characterize their structures by ^{19}F NMR. As a result, the quantification of the linear chain and ten CF_3 branched isomers present in technical PFOS proved possible.

2. Materials and methods

2.1. Synthesis/separation

A commercial sample of PFOSF (Sigma–Aldrich) was converted into secondary sulfonamides (PFOSamide) as described elsewhere (Lyapkalo et al., 2002) and the resulting mixture of isomers was separated by a combination of crystallisation and preparative-scale

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HPLC. Nine different isomers (**1b–9b**) were isolated in purities ranging from *ca* 90–99%. Two isomers (**10b** and **11b**) were obtained only as a mixture in a ratio of *ca* 5:3, with **10b** predominating. The normal chain sulphonamide was purified to better than 99% as determined by ^{19}F NMR spectroscopy.

Technical potassium perfluorooctanesulfonate was obtained from Matrix Scientific (lot # P15D).

2.2. ^{19}F NMR experiments

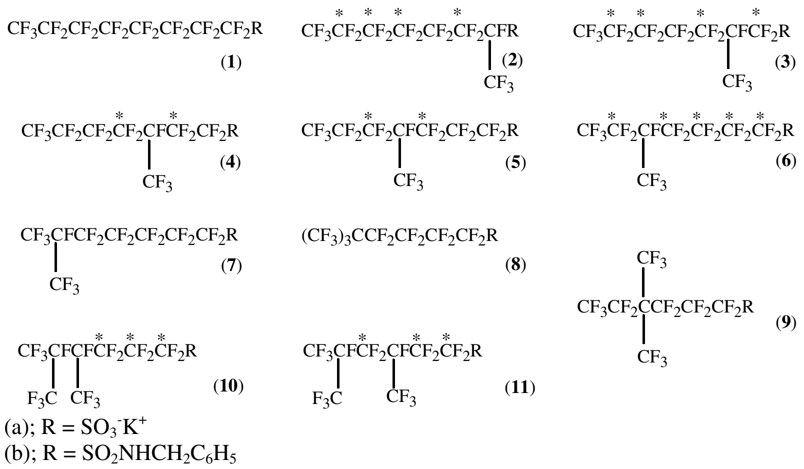
^{19}F spectra for quantification of the isomers in technical PFOS were recorded at 375.50 MHz on a Bruker Avance DPX 400 NMR spectrometer equipped with a Bruker SEF $^{19}F/^{1}H$ dual probehead. Five hundred scans were obtained in 64 K data points over a 60.240 kHz spectral width (0.544 s acquisition time) using a 30° flip-angle pulse with ^{1}H decoupling. The ^{19}F 90° pulse width was 8.5 μs. A 10 s relaxation delay was employed. The free induction decays (FIDs) were processed using exponential multiplication (line-broadening 1 Hz) before Fourier transformation.

2D ^{19}F COSY spectra was recorded in the absolute value mode using the pulse sequence 90°-t_1-45°-ACQ. The spectra were acquired in 100 scans for each of 512 FIDs that contained 4 K data points in F2 over a 45.977 kHz spectral width. A 1.0 s relaxation delay was employed between acquisitions. Zero-filling in F1 produced a 4 K × 1 K data matrix. During 2 D Fourier transformation, a sine-bell window function was applied to both dimensions and forward linear prediction in F1. The transformed data were then symmetrized.

All PFOSamide isomers were dissolved in methanol-d_4 (CDN Isotopes). Chemical shifts are reported in ppm relative to hexafluorobenzene (Sigma–Aldrich) using the signal at −169 ppm as internal reference (Cornelissen et al., 2000).

3. Results and discussion

The structures of the eleven isomeric PFOS derivatives (**1b–11b**) analyzed by ^{19}F NMR are shown in Scheme 1 and their NMR spectra are summarized in Table 1. Partial spectra for the



Scheme 1. Structures of the 11 major PFOS isomers (∗ signifies that the ^{19}F NMR signal exists as a clearly resolved AB quartet).

Table 1
^{19}F NMR of the of the 11 major isomers separated from a technical mixture of PFOSamide

Compound[a]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Branched CF_3
1b	−117.84	−125.08	−126.31	−126.41	−126.58	−127.40	−130.95	(−86.02)[b]
2b	−172.20	−117.81[c]	−124.43	−126.25[c]	−127.41[c]	−131.00[c]	−86.03	−75.24
		−117.51		−126.05	−127.27	−130.88		
3b	−108.01[c]	−186.80	−117.05[c]	−124.30	−127.06[c]	−130.83[c]	−85.98	−74.74
	−107.47		−116.15		−126.98	−130.73		
4b	−116.13	−115.10[c]	−189.68	−116.83[c]	−125.18	−130.62	−85.86	−75.12
		−114.85		−116.39				
5b	−117.62	−123.01	−116.53[c]	−190.03	−117.37[d]	−128.87	−85.79	−75.12
			−116.30		−117.01			
6b	−117.79[c]	−124.84[c]	−124.24[c]	−117.30[d]	−189.81	−121.11[c]	−85.17	−75.55
	−117.68	−124.71	−124.41			−120.88		
7b	−117.85	−125.03	−125.90	−125.26	−119.54	−190.74	−76.90[e]	−76.90[e]
8b	−117.61	−124.23	−121.45	−108.62	−66.52[f]			
9b	−117.12	−119.98	−105.48		−110.30	−83.01		−64.06[e]
10b	−118.09[c]	−123.21[c]	−115.41[c]	−179.81	−184.86	−74.09[e]		−75.00
	−116.97	−122.27	−111.27					
11b	−116.47[c]	−115.52[c]	−187.56	−109.43[c]	−187.18	−77.17[e]		−75.15
	−115.91	−113.95		−108.85				

[a] The numbering of the carbon chain is as follows: C(7)–C(6)–C(5)–C(4)–C(3)–C(2)–C(1)–R (R = $SO_2NHCH_2C_6H_5$).

[b] This actually is the terminal CF_3 in the linear compound (**1**).

[c] AB pattern observed due to chirality in the structure; $^{2}J_{FF}$ *ca* 300 Hz; actual shift positions calculated from observed values using “Spinworks” provided by Dr. K. Marat, University of Manitoba.

[d] AB system with outside lines visible but inside lines overlapping to give a broad singlet because of extensive additional coupling.

[e] This signal arises from the two equivalent CF_3 groups.

[f] This signal (quintet, $^{4}J_{FF} = {}^{5}J_{FF} = 13$ Hz) arises from the three equivalent CF_3 groups on the *t*-butyl moiety.