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Document Control Office (DCO)
Office of Pollution Prevention and Toxics (OPPT)
US Environmental Protection Agency
EPA East, Room 6428
1201 Constitution Avenue, MW
Washington DC 20460

Dear Sir or Madam:

During the July 9, 2003 meeting of the Fluoropolymers Technical Workgroup there was a request for information on the physical/chemical properties of PFOA. This information is attached. In addition, a summary of environmental fate study results is included in the attachment to augment the understanding of environmental behavior of this substance.

This document should be considered an addition to the P-Chem properties for fluoropolymers data request made in Item 2 on page 11 of the Preliminary Framework document published by EPA on May 20, 2003. A reference of this submittal should be placed in the Electronic Docket OPPT-2003-0012.

Sincerely,

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Attachment

PERFLUOROOCCTANOIC ACID

Physiochemical Properties¹ and Environmental Fate Data

PERFLUOROOCCTANOIC ACID - PHYSICAL AND CHEMICAL PROPERTIES¹

Chemical Identity

Chemical Name: Perfluorooctanoic Acid

Molecular formula: C₈ H F₁₅ O₂

Structural formula: F-CF₂-CF₂-CF₂-CF₂-CF₂-CF₂-CF₂-C(=O)-X,

The free acid and some common derivatives have the following CAS numbers:

The perfluorooctanoate anion does not have a specific CAS number.

Free Acid (X = OM⁺; M = H) [335-67-1]

Ammonium Salt (X = OM⁺; M = NH₄) [3825-26-1]

Sodium Salt (X = OM⁺; M = Na) [335-95-5]

Potassium Salt (X = OM⁺; M = K) [2395-00-8]

Silver Salt (X = OM⁺; M = Ag) [335-93-3]

Acid Fluoride (X = F) [335-66-0]

Methyl Ester (X = CH₃) [376-27-2]

Ethyl Ester (X = CH₂-CH₃) [3108-24-5]

Synonyms: 1-Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-PFOA

Ammonium perfluorooctanoate (APFO) is the Fluorinated Polymerization Aid (FPA) most commonly used in the production of many fluoropolymers and fluoroelastomers. APFO has several synonyms including C-8 acid, FC 143, and perfluoro-ammonium octanoate. The free acid, perfluorooctanoic acid, is often called PFOA. A more complete description of physical and other properties of this and other (FPA)s may be found in *Fluorinated Surfactants*².

Thermal Behavior

Perfluorooctanoic acid has a fairly low melt point of 45 – 50°C, with slight sublimation reported to occur at 40°C³. The reported vapor pressure of PFOA, 10 mm Hg, appears high for a low melting solid when compared to other low melting solids (chloroacetic acid: solid; MP = 61 to 63 /C; BP = 189 /C; VP = 0.1 kPa (0.75 mm Hg) @ 20 /C; NIOSH), but is consistent with other perfluorinated compounds with similar boiling points (perfluorobutanoic acid BP = 120 /C, VP 10 mm Hg @ 20 /C)⁴. The vapor pressure was measured at an elevated temperature (inadvertently omitted from the report).

Perfluorooctanoic acid is typically handled as a liquid at 65 /C⁵.

While it may be expected that conversion of the PFOA acid to a salt should reduce its volatility, ammonium perfluorooctanoate, the most commonly used salt of PFOA, shows volatility at fairly low temperatures. The vapor pressure of ammonium perfluorooctanoate (APFO) was reported to be approximately 7 X 10⁻⁵ mm Hg at 20°C.⁶

A study of weight loss behavior by thermogravimetric analysis of various salts of perfluorooctanoic acid illustrates the differences in thermal behavior⁷. For example, the ammonium salt began to show loss of sample weight in the 50-100°C range (20% loss under the conditions used at 167 °C), while the sodium salt did not show weight loss until about the 200-250°C range (20% weight loss at 298° C). The ammonium salt begins to

sublimate at 130°C with 20% of the weight of the sample t lost by 169°C. Other salts (Cs, K, Ag, Pb, Li) do not demonstrate similar weight loss until 237°C or higher.⁸ Decomposition of different salts produces perfluoroheptene (loss of metal fluoride and carbon dioxide). This occurs at 320°C for the sodium salt and at 250-290 /C for the silver salt⁴.

Behavior in Water

As expected, the solubility of perfluorooctanoic acid and other salts is complex and can involve the formation of micellar solutions and liquid crystal phases. Phase diagrams have been published for ammonium perfluorooctanoate.⁸ The free acid of PFOA is expected to completely dissociate in water. In aqueous solutions, individual molecules of PFOA anion loosely associate on the water surface and partition between the air / water interface. Several reports note that PFOA salts self-associate at the surface, but with agitation they disperse and micelles form at higher concentrations^{9, 10 & 11}. Water solubility has been reported for PFOA, but it is unclear whether these values are for a microdispersion of micelles, rather than true solubility.

Due to these same surface-active properties of PFOA, and the test protocol for the OECD shake flask method, PFOA is anticipated to form multiple layers in octanol/water Therefore, an n-octanol/water partition coefficient cannot be determined.

The PFOA derivative having the greatest use is the ammonium salt (APFO; CAS No. 3825-26-1). The water solubility of APFO has been inconsistently reported. One 3M study reported the water solubility of APFO to be > 10%. It was noted in an earlier study that at concentrations of 20 g/L, the solution “gelled” (3M, 1979). This latter result seems surprising low for a salt in light of Apollo Scientific selling a 31% aqueous solution of APFO. One author reported the APFO partition coefficient $\log P_{ow} = 5$. Another author reported an estimated APFO $\log P_{ow} = -0.9$. This value might not be accurate due to the estimation method used¹². Again, the anticipated formation of an emulsified layer between the octanol and water surface interface would make determination of $\log K_{ow}$ impossible.

Physicochemical Properties

The available physicochemical properties for the PFOA free acid are:

Molecular weight: 414⁵

Melting point: 45 – 50 /C⁵

Boiling point: 189 – 192 /C / 736 mm Hg⁵

Vapor pressure: 10 mm Hg @ 25 /C (approx.) (**Exfluor MSDS**)

Water solubility: 3.4 g/L (telomeric [MP = 34 /C ref. 0.01 - 0.02 mol/L ~4 - 8 g/L) (**MSDS from Merck, Fischer, and Chinameilan Internet sites**)

pKa: 2.5 (**USEPA AR226- 0473**)

pH (1g/L): 2.6 (**MSDS Merck**)

Methanol solubility: >10% by weight (**3M Study 2001**)

Acetone solubility: >10% by weight (**3M Study 2001**)

The physicochemical properties of PFOA and its common derivatives are summarized in Table 1.

Table 1. Reported Physicochemical Properties

Compound	CAS REG#	MP	BP	VP	Sol.-H2O	Log P*
R-C(=O)Cl	335-64-8		131°C			
R-CO2H	335-67-1	55°C	189°C	10 mm Hg	3.4 g/L	
R-CO2-NH4+	3825-26-1	130°C (sub)	Sublimes	1 x 10E - mm Hg	20 g/L gels	
R-C(=O)OMe	376-27-2		159°C			
pH (1 g free acid/L water) = 1.5 – 2.5			Free acid pKa is approximately 0.6			
Sodium or Silver salts of PFOA decompose above 250°C to generate perfluoroolefins.						

Surfactants traditionally emulsify octanol and water

The environmental fate study results are shown in Table 2.

Table 2. PFOA Environmental Fate Data

Product	Cation	% PFOA in product	Parameter	Results	Comments	Year Tested
FC-143	NH ₄		Soil Sorption (Brill sandy loam soil)	K = 0.21, Koc = 14	Highly mobile; 3M Study	1978
FC-143	NH ₄	97-100	30-day photolysis exposure	No evidence of degradation	3M Study	1979
FC-143	NH ₄	95.2	Direct and indirect photolysis	Minimum indirect photolysis 1/2 life at 25°C = >349 days	No evidence of direct or indirect loss of PFOA was observed; 3M Study	2001
FC-143	NH ₄	95.2	Hydrolysis at pH 1.5, 5.0, 7.0, 9.0	hydrolytic 1/2 life at 25°C = > 97 days	PFOA loss was pH independent; 3M Study	2001
FC-143	NH ₄	97-100	log Kow	-0.9	Calculated; 3M Study	1981
FC-143	NH ₄	97-100	BCF - fathead minnow	1.8	PFOA conc. was calculated from total F ⁻ conc. After 15-days depuration, fish tissue conc dropped from 47 ppm to 8 ppm (wet weight); 3M Study	1995
FC-143	NH ₄	97-100	Biodegradation (ABS/LAS shake culture)	No evidence of biodegradation	2.5 month exposure. Inoculum mixture of municipal and 3M industrial activated sludge. 3M Study	1978
FC-143	NH ₄	97-100	Ready biodegradability - CBOD-20/COD	Nil	3M Study	1980
FX-1001	H	95-98	Ready biodegradability - CBOD-20/COD	Nil	3M Study	1985

Table 2. PFOA Environmental Fate Data (cont.)

Product	Cation	% PFOA in product	Parameter	Results	Comments	Year Tested
FC-126	NH ₄	78-93	Ready biodegradability - CBOD-20/COD	0.86	3M Study	1987
FC-143	NH ₄	95.2	18-Day aerobic biodegradability with measured conc.	No evidence of biodegradation	3M Study	2001

¹ Information taken from the *Guide to the Safe Handling of Fluoropolymer Dispersions*, Fluoropolymers Manufactures Group, Society of Plastics Industry, Washington DC, October 2001, and the *Preliminary Risk Assessment of the Developmental Toxicity Associated with Exposure to Perfluorooctanoic Acid and its Salt*, US EPA, OPPT, Risk Assessment Office, April 10, 2003

² Kissa, Erik *Fluorinated Surfactants*; Marcel Dekker: New York, 1994

³ Nakayama, Haruo *Bull. Chem. Soc. Jpn.* 1967, 40, 1592-95.

⁴ Beilstein (1975) Beilstein Handbook 4th Work Volume 2 Part 2 page 994

⁵ 3M data sheet for FC-26

⁶ Griffith, F. D. and Long, J. E. *Am. Ind. Hyg. Assoc. J.* 1980, 41, 576-83.

⁷ Lines, D. and Sutcliffe, H. *J. Fluorine Chem.* 1984, 25(4), 505-12.

⁸ Tiddy, G. J. T. *J. Chem. Soc., Faraday Trans. I* 1972, 68, 608-12.

⁹ Simister, EA; Lee, EM; Lu, JR; Thomas, RK; Ottewill, RH; Rennie, AR; Penfold, J. (1992). Adsorption of ammonium perfluorooctanoate and ammonium decanoate at the air-solution interface. *J Chem Soc, Faraday Trans* 88(20):3033-41.

¹⁰ Calfours, J; Stilbs, P. (1985) Solubilization in sodium perfluorooctanoate micelles: a multicomponent self-diffusion study. *Colloid Interface Sci* 103:332-336.

¹¹ Edwards, PJB; Jolley, KW; Smith, MH; et al. (1997) Solvent isotope effect on the self-assembly liquid crystalline phase behavior in aqueous solutions of ammonium pentadecafluorooctanoate. *Langmuir* 13(10):2665-2669.

¹² Hansch, C; Leo, A; Eds. (1979) The fragment method of calculated partition coefficients. In: *Substituent Constants for Correlation Analysis and Chemistry and Biology*, Chapter IV. John Wiley and Sons, Inc.