

Chemistry, Properties, and Uses of Commercial Fluorinated Surfactants

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Abstract Fluorinated surfactants have been commercially available since the 1950s. The first available were perfluoroalkyl sulfonic acids. The unique properties e.g., surface tension lowering in aqueous systems, high chemical and thermal stability of these acids and their derivatives when used at low concentrations resulted in their widespread use in industrial processes and consumer uses. The most common commercially produced perfluorinated surfactants are the perfluoroalkyl acids.

Subsequently, additional commercial processes were developed for synthesis of a range of per- and poly-fluorinated surfactants whose unique properties make them largely irreplaceable in many applications. The widespread use and disposal and the high stability of the perfluoroalkyl acids, which do not breakdown readily either abiotically or biotically in the environment, has resulted in widespread presence of PFAAs in the environment. This caused commercial production to shift toward short chain alternatives and new fluorinated moieties such as the per- and poly-fluorinated ethers. Clearly, there remains a need for fluorinated surfactants in many industries to obtain the beneficial performance properties of these substances that cannot be achieved with other types of surfactants.

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The aim of this chapter is to provide an overview of the commercially relevant chemistry, properties, and uses of commercial fluorinated surfactants.

Keywords Chemical production • Fluorinated surfactants • Physico chemical properties

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Abbreviations

ABS	Acrylonitrile butadiene styrene
AFFF	Aqueous film-forming foams
CMC	Critical micelle concentration
ECF	Electrochemical fluorination
EOR	Enhanced oil recovery
HFP	Hexafluoropropene
HFPO	Hexafluoropropene oxide
PBSF	Perfluorobutanesulfonyl fluoride
PDSF	perfluorodecane sulfonyl fluoride
PEM	Polymer electrolyte membrane
PFAAs	Perfluoroalkyl acids
PFCA	Perfluoroalkyl carboxylic acid
PFCA _s	Perfluoroalkyl carboxylic acids

PFDS	Perfluorodecane sulfonate
PFOS	Perfluorooctane sulfonate
PFPA	Perfluoroalkyl phosphonic acid
PFPIA	Perfluoroalkyl phosphinic acid
PFSA	Perfluoroalkyl sulfonic acid
PH _x SF	perfluorohexane sulfonyl fluoride
POSF	Perfluorooctane sulfonyl fluoride
TFE	Tetrafluoroethylene

1 Introduction

The surfactant universe includes a wide variety of substances from natural to synthetic that contain functional groups which provide specific performance properties for a plethora of valuable industrial and consumer uses. Fluorinated surfactants are a specific class of surfactants whose properties are derived from substitution of at least one hydrogen atom along the carbon backbone that makes up the hydrophobic part of the surfactant with fluorine [1–7]. The terms fluoro-surfactant, fluorinated surfactant, and fluorinated tenside are synonyms that describe a broad and diverse group of surfactants. The extent and location of fluorine substitution in the surfactant affect the surfactant properties. For example, fluorinated surfactants with a terminal $-\text{CF}_3$ group differ from fluorinated surfactants with a hydrogen-containing terminus [2]. A polyfluorinated surfactant is one in which more than one, but not all hydrogen atoms are substituted with fluorine. The carbon–fluorine bond is very strong and the perfluoroalkyl functional group, $\text{F}(\text{CF}_2)_n-$, is both hydrophobic and oleophobic [8]. Perfluorinated surfactants represent the ultimate type of fluorinated surfactant, where *all* hydrogen bound to carbon is replaced with fluorine except those hydrogen atoms whose substitution would modify the nature of any functional groups present [9].

Fluorinated surfactants have been commercially available since the 1950s. The first available were perfluoroalkyl sulfonates (e.g., perfluorooctane sulfonate, $\text{C}_8\text{F}_{15}\text{SO}_3^-$, PFOS) and perfluoroalkyl carboxylic acids (e.g., perfluorooctanoic acid, $\text{C}_7\text{F}_{15}\text{COOH}$, PFOA) manufactured using the electrochemical fluorination (ECF) process [10]. The unique properties (e.g., surface tension lowering in aqueous systems, high chemical and thermal stability) of these acids and their derivatives when used at low concentrations resulted in their widespread use in industrial processes and consumer uses [11–13]. The most common commercially produced perfluorinated surfactants are the perfluoroalkyl acids (PFAAs):

Perfluoroalkyl acids

General name	Acronym	Structure
Perfluoroalkyl sulfonic acid	PFSA	$\text{F}(\text{CF}_2)_n\text{SO}_3\text{H}$
Perfluoroalkyl carboxylic acid	PFCA	$\text{F}(\text{CF}_2)_n\text{CO}_2\text{H}$
Perfluoroalkyl phosphonic acid	PFPA	$\text{F}(\text{CF}_2)_n\text{P}(=\text{O})(\text{OH})_2$
Perfluoroalkyl phosphinic acid	PFPIA	$\text{F}(\text{CF}_2)_n\text{P}(=\text{O})(\text{OH})$



Fig. 1 Schematic of a fluorinated surfactant

Subsequently, additional commercial processes were developed for synthesis of a range of per- and polyfluorinated surfactants whose unique properties make them largely irreplaceable in many applications. The widespread use and disposal and the high stability of the PFAAs, which do not break down readily either abiotically or biotically in the environment, has resulted in widespread presence of PFAAs in the environment [14–16]. The aim of this chapter is to provide an overview of the commercially relevant chemistry, properties, and uses of commercial fluorinated surfactants.

2 Chemistry of Fluorinated Surfactants

An understanding of the chemistry of fluorinated surfactants must consider three distinct structural aspects: (1) the hydrophobic/oleophobic “tail” that contains a high proportion of fluorine, (2) the hydrophilic group, and (3) the “spacer” organic group linking these two portions of the surfactant together (Fig. 1). As with hydrocarbon surfactants, the valuable and important fluorinated surfactants include a diverse range of hydrophilic groups: (a) anionic, for example, sulfonates, sulfates, carboxylates, and phosphates, (b) cationic, for example, quaternary ammonium, (c) nonionic, for example, polyethylene glycols, acrylamide oligomers, and sugars, and (d) amphoteric, for example, betaines and sulfobetaines [2].

The practical and commercially valuable range of the hydrophobic/oleophobic “tail” of the fluorinated surfactant is limited [3, 5, 6]. Either perfluoroalkyl, $F(CF_2)_n-$ or R_F- , or perfluoropolyether, $(R_FO)_n(R_FO)_m-$, groups are the hydrophobic/oleophobic portion of most commercially available fluorinated surfactants. Perfluoroalkyl-containing fluorinated surfactants generally originate from either (1) ECF with HF [4] or (2) telomerization of tetrafluoroethylene (TFE) [17]. Perfluoropolyether-based fluorinated surfactants typically originate from either (1) oligomerization of hexafluoropropene oxide (HFPO), (2) photooxidation of TFE or hexafluoropropene (HFP) [18], or (3) oligomerization of fluorinated oxetanes [19].

2.1 Electrochemical Fluorination

The ECF of organic compounds using anhydrous HF was the first significant commercial process for manufacturing ECF-based fluorinated surfactants [4, 10, 20, 21].

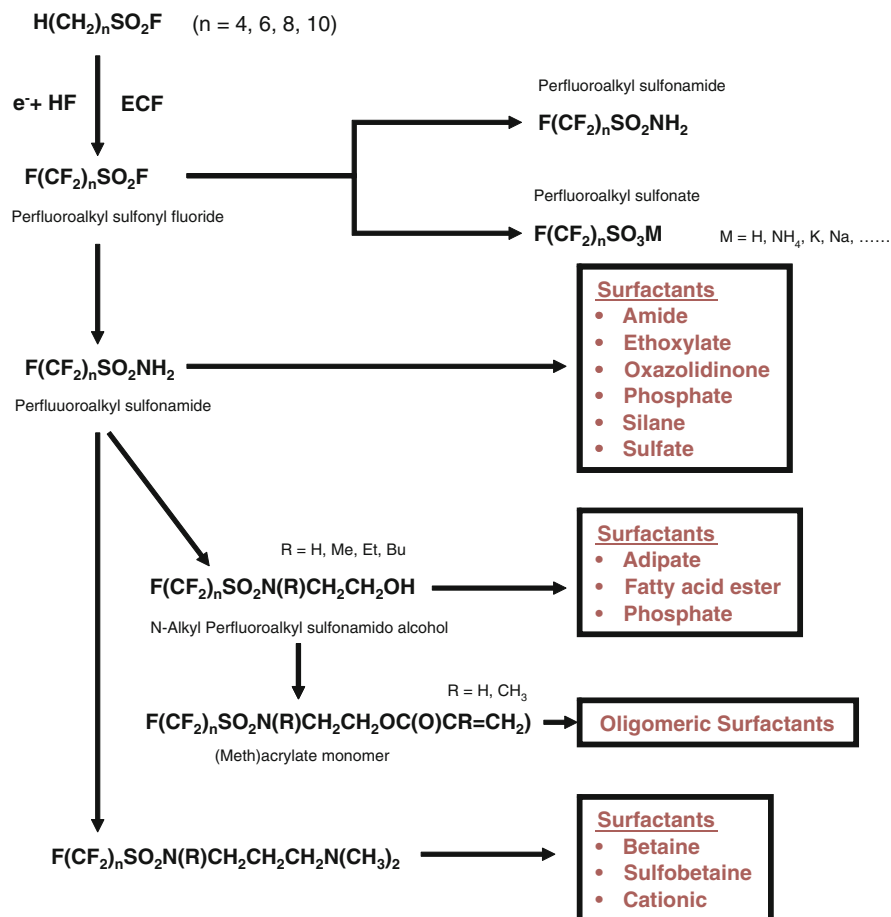


Fig. 2 Synthesis of ECF-based fluorinated surfactants

Typically, a hydrocarbon sulfonyl fluoride ($\text{R-SO}_2\text{F}$, for example, $\text{C}_4\text{H}_9\text{SO}_2\text{F}$ or $\text{C}_8\text{H}_{17}\text{SO}_2\text{F}$) is transformed into the corresponding perfluoroalkyl sulfonyl fluoride ($\text{R}_f\text{-SO}_2\text{F}$, for example, $\text{C}_4\text{F}_9\text{SO}_2\text{F}$ or $\text{C}_8\text{F}_{17}\text{SO}_2\text{F}$). The perfluoroalkyl sulfonyl fluoride is the fundamental raw material which is further processed to yield fluorinated surfactants (Fig. 2). Commercially relevant perfluoroalkyl-sulfonyl fluorides are derived from 4, 6, 8, and 10 carbon starting materials yielding perfluorobutanesulfonyl fluoride (PBSF), perfluorohexane sulfonyl fluoride (PH_xSF), perfluorooctane sulfonyl fluoride (POSF), and perfluorodecane sulfonyl fluoride (PDSF), respectively. In the ECF process, fragmentation and rearrangement of the carbon skeleton occurs and significant amounts of cleaved, branched, and cyclic structures are formed resulting in a complex mixture of fluorinated materials of varying perfluoroalkyl carbon chain length and branching as well as trace levels of perfluorocarboxylic acid impurities [2, 20, 22]. The most basic surfactant derived

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