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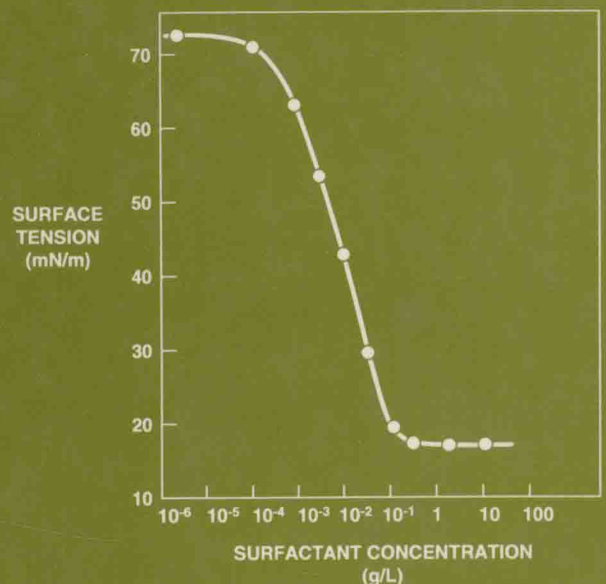
volume 50

FLUORINATED SURFACTANTS

Synthesis • Properties • Applications



Erik Kissa

FLUORINATED SURFACTANTS

Synthesis • Properties • Applications

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Preface

Fluorinated surfactants are truly the super surfactants. Fluorinated surfactants can decrease the surface tension of water below the lower limit reached by hydrocarbon-type surfactants. The perfluorinated hydrophobe is extremely resistant to chemical attack, and fluorinated surfactants can be used in media where conventional surfactants do not survive. Since a perfluoroalkyl chain is not only hydrophobic but oleophobic, fluorinated surfactants can serve as oil and fat repellents. Compounds consisting of a fluorinated chain and a hydrocarbon group can function as surfactants in hydrocarbon media. Because of their unique properties, fluorinated surfactants are indispensable in certain practical applications and of great theoretical interest for the study of surfactants and micellar systems.

Chapter 1 presents an overview of fluorinated surfactants. The synthesis of fluorinated surfactants is discussed in Chapter 2. Since the space limitations precluded a detailed description of processes, patent citations are augmented by references to *Chemical Abstracts*. Physical and chemical properties are reviewed in Chapter 3. Chapters 4–7 are devoted to the theory of fluorinated surfactants: liquid-vapor and liquid-liquid interface (Chapter 4), solid-liquid interface (Chapter 5), solutions of fluorinated surfactants (Chapter 6), and the structure of micelles and mesophases, including mixed surfactant systems, in Chapter 7. The practical application of fluorinated surfactants is the subject of Chapter 8. Various applications are listed in alphabetical order for easy access to information. Chapter 9 reviews analytical and physical methods for the investigation of fluorinated surfactants. Chapter 10 examines the environmental and toxicological aspects, including the use of fluorinated surfactants in biological systems.

Because of my intention to write a stand-alone book, material dealt with in other monographs has been included. Related theories and principles are presented along with references to the literature for those who wish to study the fundamental theories in depth. Some discussion of hydrocarbon-type surfactants is given so they can be compared with fluorinated surfactants.

Several computer-aided literature searches were conducted. Ongoing research on fluorinated surfactants is very active, and while the book was being written new material had to be constantly reviewed. An effort was made to keep all chapters up to date.

Since the book was written at home after regular working hours, I am immensely grateful to my wife, Selma, whose support and patience made this book possible.

I am indebted for valuable comments and suggestions to Du Pont chemists who read the chapters in which they have expertise: Drs. J. E. Dowd, T. A. Liss, and J. F. Neumer (synthesis), K. S. Prowse (applications), M. W. Duch (ESCA), J. T. Cronin (IR), A. Foris (NMR), J. R. Valentine (MS), B. E. Baker (toxicology), R. C. Bergman and S. Raynolds (intravascular oxygen carriers). I am also grateful to my son Erik H. Kisa, M.D., for reviewing the chapter on blood substitutes.

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Erik Kissa

FLUORINATED SURFACTANTS

Contents

1
Structure of Fluorinated Surfactants

1.1 INTRODUCTION

Surfactants have a very important role in our everyday life. Surfactants are essential in biological systems and industrial processes. Our food, cosmetics, medicine, and household items, such as soap and detergents, contain surfactants. The wide variety of surfactant applications has required different types of surfactants and a large number of surfactant structures is available for the specific need. The literature on surfactants is voluminous.

The word *surfactant* is an abbreviation of the more descriptive term *surface-active agent*. A surfactant is a substance which, even at low concentrations, effectively lowers the surface tension of its medium by selective adsorption on the interface. A surfactant can be a pure chemical compound or a mixture of homologues or different chemical compounds. The characteristic feature of surfactants is their efficiency in lowering surface tension. The surface tension of a liquid can be lowered by mixing it with another liquid of lower surface tension. For example, one part of ethanol added to four parts of water decreases the surface tension of water from 73 mN/m to below 40 mN/m. However, only 0.1% of a typical surfactant is needed for the same surface tension reduction. The efficiency of surfactants in lowering surface tension is related to selective adsorption of the surfactant at the interface. The adsorption, in turn, is a result of the amphiphilic nature of the surfactant.

The term amphiphilic or amphipathic, as it is sometimes called, implies attraction to two different kinds of media. The surfactant structure can be described as consisting of two parts with vastly different solution characteristics: a "solvent-soluble" lyophilic part and a "solvent-insoluble" lyophobic part.

Conventional surfactants consist of a water-soluble hydrophilic part and a water-insoluble hydrophobic part which is lipophilic, compatible with fats and hydrocarbons. The hydrophobe is usually a hydrocarbon group, but surfactants containing oxygen, nitrogen, sulfur, silicon, and/or halogens are also used.

In fluorinated surfactants the hydrophobic part of the surfactant molecule contains fluorine. At least one hydrogen atom in the hydrophobic segment of a surfactant has been replaced by fluorine. Both the extent of fluorination and the position of fluorine atoms in the surfactant molecule affect the characteristics of the surfactant. Hence fluorinated surfactants can be classified as perfluorinated surfactants or partially fluorinated surfactants. In perfluorinated surfactants all hydrogens in the hydrophobic segment have been replaced by fluorine. In partially fluorinated surfactants the hydrophobic part of the surfactant molecule contains both fluorine and hydrogen atoms. The location and the number of fluorine atoms in the partially fluorinated hydrophobe are important. Partially fluorinated surfactants with a terminal CF_3-group differ in their characteristics from partially fluorinated surfactants with a hydrogen-containing terminal group.

Substitution of fluorine for hydrogen changes the properties of a surfactant drastically [1–12]. The hydrophobic part of the fluorinated surfactant not only repels water but repels oil and fat as well. Hence fluorinated surfactants exhibit both water and oil repellency when adsorbed on substrates such as textiles or paper. Fluorinated surfactants are much more surface active than their hydrocarbon counterparts. Fluorinated surfactants can lower surface tension of aqueous systems to below 20 mN/m and are effective at very low concentration. Only 10 ppm of a fluorinated surfactant may be needed to lower the surface tension of water to 40 mN/m. Fluorinated surfactants exhibit surface activity in organic systems and are stable to heat, acids, and bases, as well as reducing and oxidizing agents. On the negative side is the higher price of fluorinated surfactants, but this is at least partially offset by the small quantities usually needed. Because of their unique properties, fluorinated surfactants are irreplaceable in many applications.

The term *fluorinated surfactant*, although widely used, can be misleading, since it implies that the hydrocarbon segment of a surfactant has been fluorinated. This, of course, is not the real synthetic route to surfactants with a fluorine-containing hydrophobe. The author therefore prefers the shorter term *fluorosurfactant*, in analogy to the frequently used terms *fluorochemical* and *fluorocarbon*. However, the term fluorinated surfactants is conventional and, consequently, the title of this book.

Some surfactants have counterions which contain fluorine but do not have fluorine in their hydrophobic part. Although such surfactants do not really belong to the class of fluorinated surfactants proper, the presence of fluorine in the counterion affects the behavior of the surfactant. Such surfactants have therefore been included in this book.

1.2 STRUCTURAL FEATURES OF FLUORINATED SURFACTANTS. THE HYDROPHOBE

To understand how surfactants function and to select a surfactant for a specific purpose it is necessary to classify surfactants according to their structural features.

Like all surfactants, fluorinated surfactants are either ionic or nonionic. Ionic surfactants can, unlike nonionic surfactants, dissociate into ions in an aqueous medium. The hydrophobic part can belong to a negative or positive ion. Some surfactants have negatively and positively charged functional groups on the same backbone. The surfactants can therefore be classified into four types:

Anionic surfactants—the hydrophobic part is an anion, for example, $R_fCOO^-Na^+$, where R_f is a fluorine-containing hydrophobe.

Cationic surfactants—the hydrophobic part is a cation, for example, $C_7F_{15}CONH(CH_2)_3N^+(CH_3)_3I^-$.

Amphoteric surfactants—have at least one anionic and one cationic group at their isoelectric point.

Nonionic surfactants—do not dissociate into ions, for example, $C_7F_{15}CH_2CH_2O(CH_2CH_2O)_nH$. A special class of nonionic fluorinated surfactants are compounds which do not have a hydrophile but consist of an oleophobic (fluorinated) segment and a oleophilic segment (see Sec. 1.8).

The structure of the hydrophobe of an anionic fluorinated surfactant can be varied more extensively than the structure of the hydrophile. The hydrophobe can be a fully or partially fluorinated alkyl group having a linear or a branched alkyl chain. The hydrophobe can have an aromatic group or contain other elements (O, N, Cl, S, and Si) as well, as shown with the following examples:

C, H, F

$C_nF_{2n+1}-$

$C_nF_{2n+1}CH_2CH_2-$

C, H, F, O

$C_nF_{2n+1}OCF_2CF_2-$

$C_nF_{2n+1}OC_6H_4-$

C ,H, F, O, N

$C_nF_{2n+1}CONH(CH_2)_3N<$

C ,H, F, O, S

$C_nF_{2n+1}SO_2NH(CH_2)_3N<$

C, F, Cl

$CF_3Cl_2(CF_2CFCl)_{n-1}CF_2-$

C, F, Si

$C_8F_{17}CH_2CH_2Si(CH_3)_2-$

The hydrophobes of partially fluorinated surfactants contain both fluorine and hydrogen atoms. Unlike the hydrophobe of hydrocarbon surfactants, the partially fluorinated hydrophobe consists of two mutually phobic parts which are not compatible. Partially fluorinated surfactants therefore exhibit anomalies in macroscopic characteristics, such as the critical micelle concentration (cmc), and in microscopic phenomena as well.

Partially fluorinated surfactants have several advantages over perfluorinated surfactants. The hydrocarbon segment provides solubility in more commonly used solvents, lowers the melting point of the surfactant, reduces volatility, and decreases the acid strength of fluorinated acids [13].

Hydrocarbon-type surfactants with fluorinated counterions are not truly fluorinated surfactants, because the surface-active ion is not fluorinated. However, fluorination of the counterion affects the solution characteristics of the surfactant and has been the subject of several investigations. Moss and coworkers [14,15] used the CF_3SO_3- anion as a counterion for a sulfonium methylating agent and a hydroperoxy surfactant. Hoffmann et al. [16,17] investigated surfactant association in solutions of dodecylammonium and tetradecylammonium trifluoroacetates and tetradecylpyridinium perfluorobutyrate. Sugihara et al. [18] studied the solubility and cmc of dodecylammonium perfluorocarboxylates in water. The effect of the counterion (trifluoroacetate, pentafluoropropionate, and heptafluorobutyrate) hydrophobicity on solubility, cmc, and the Krafft point were determined.

1.3 ANIONIC FLUORINATED SURFACTANTS

Ionic surfactants dissociate in water and form a surface-active ion with an oppositely charged counterion. The surface-active ions of anionic surfactants bear a negative charge. Anionic fluorinated surfactants can form water-insoluble ion pairs with cationic species and are usually not compatible with most cationic surfactants.

Anionic surfactants are the most important class of fluorinated surfactants. Based on the hydrophile structure, anionic fluorinated surfactants can be divided into four main categories:

Carboxylates	$R_fCOO^-M^+$
Sulfonates	$R_fSO_3^-M^+$
Sulfates	$R_fOSO_3^-M^+$
Phosphates	$R_fOP(O)O_2^{--}M_2^+$

where R_f is a fluorine-containing hydrophobe and M^+ an inorganic or an organic cation. Some anionic surfactants contain nonionic hydrophilic polyoxyethylene segments which increase their solubility and compatibility with cationic or amphoteric surfactants.