



Effects of chemical structure on the dynamic and static surface tensions of short-chain, multi-arm nonionic fluorosurfactants



Thomas Schuster^a, Joseph W. Krumpfer^a, Steffen Schellenberger^b, Reiner Friedrich^b, Markus Klapper^{a,*}, Klaus Müllen^a

^aMax Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

^bMerck KGaA, Frankfurter Straße 250, 64293 Darmstadt, Germany

ARTICLE INFO

Article history:

Received 18 March 2014

Accepted 23 April 2014

Available online 2 May 2014

Keywords:

Fluorosurfactants

Static surface tension

Dynamic surface tension

Multi-arm structures

Structure–property relations

Non-ionic surfactants

Short perfluoroalkyl chains

ABSTRACT

Fluorinated surfactants with short perfluoroalkyl chains (R^F) as potential substitutes for the environmentally questionable, long R^F systems are presented. Three types of nonionic hydrophilic-fluorophilic amphiphiles are synthesized and evaluated based on surface activity in equilibrated (static) and non-equilibrated (dynamic) states. Furthermore, several mono- and disaccharide-based fluorosurfactants are also examined as potential non-bioaccumulative alternatives. A correlation between the chemical structure and resulting surface properties is made by comparing R^F length, number and size, alkyl-spacer, and hydrophilic moieties. Based on dynamic and static surface tension experiments, the effects of surfactant structure are summarized to provide a basis for the future design of fluorosurfactants. We have found that surfactants with more perfluorinated chains tend to have a higher surface tension reduction, but typically result in slower dynamic behaviors. Using the presented structural characteristics, surfactants with $R^F < 4$ can be prepared with static surface tensions as low as 18.1 mN/m or reduce surface tension within milliseconds.

© 2014 Published by Elsevier Inc.

1. Introduction

Fluorosurfactants have had many important roles in a wide range of applications, including stain resistant coatings, release agents and emulsifiers [1–5] and represent a multi-billion dollar industry [6]. However, over the last two decades, growing concerns over the environmental and health dangers presented by long perfluoroalkyl chain (R^F) chemicals has led to an increasing interest in the development of short chain ($R^F < 4$) fluorosurfactants [7–10]. This has caused many leading manufacturers of fluorosurfactants, such as 3M and DuPont, to seek alternatives to their traditional materials. For example, 3M completely discontinued their production of perfluorooctane sulfonic acid in 2002 and have since produced products based on perfluorobutane sulfonyl compounds [6,11]. In fact, due to the recent “elimination agreement” on long R^F 's [12,13] many companies throughout the world have begun

investigating short chain fluorosurfactants ($R^F < C_{6-7}$), which are not affected by the PFOA Stewardship program and are regarded as more sustainable alternatives [14–17].

Given this new demand for novel fluorosurfactants, it is useful to re-examine the role of chemical structure on surface activities, as it is known to have a profound impact on a surfactant's equilibrium and kinetic interfacial properties. Eastoe and coworkers have shown the simple difference of a CF_3 and CF_2H terminal group can noticeably affect both equilibrium and kinetic surface properties, including surface tension, surface excess and critical micelle concentration (CMC) [18]. A few specific reports of molecular structure effects on surface activities have also been reported. Several fluorosurfactants with linear, Y-shaped, and bolaform structures have been investigated [19]. In this instance, the Y-shaped surfactants were found to have static surface activities superior to those of the linear and bolaform structures. Recently, Dramé et al. reported the preparation of short-chain, two-arm fluorosurfactants with static properties equal to or better than their long, single chain counterparts [20]. That low SST can be achieved by using multi-arm surfactant structures, such as gemini surfactants, has also been reported for non-fluorinated amphiphiles [21–24].

However, in many applications, simply having a lower surface tension is often not sufficient, but rather, the speed at which the

Abbreviations: R^F -chain, perfluoroalkyl ($F(CF_2)_n-$); CMC, critical micelle concentration; SST, static surface tension; DST, dynamic surface tension; PEG, poly(ethylene glycol); PDI, polydispersity index; MALDI-ToF MS, matrix-assisted laser desorption/ionization–time-of-flight mass spectrometry; DP, degree of polymerization; HLB, hydrophilic–lipophilic balance.

* Corresponding author. Fax: +49 6131 379 350.

E-mail address: klapper@mpip-mainz.mpg.de (M. Klapper).

surface tension is reduced is equally important. For example, roll-to-roll printing applications are carried out at high speeds, where new interfaces are rapidly created by material spreading on substrates [25]. Therefore, the diffusion, adsorption and orientation of the surfactants must occur more rapidly than film drying. This is an important feature for a variety of other technical applications, such as paints and varnishes, [1–3] spray coatings [4] or *in situ* stabilization of nanoparticles [26]. In each of these examples, in which fluorosurfactants have traditionally had an important role, highly dynamic surfactants are required. Therefore, it is useful to define two decisive characteristics of these surfactants: static surface tension (SST) and dynamic surface tension (DST).

While the equilibrium properties of many fluorosurfactants have been well-studied [18,19,21], the dynamic properties have not received as much attention, particularly with regards to renewed interest in chemical structure. In non-equilibrated systems, the kinetics of diffusion and adsorption become important. For example, if a fresh interface comes into contact with a solution with a concentration below the critical micelle concentration (CMC), free surfactant molecules diffuse and adsorb to the interface, lowering the concentration of the continuous phase. For solutions at or above the CMC, aggregates provide an additional consideration. As aggregates diffuse comparatively slowly, they typically do not have a direct impact on the surfactant's interfacial properties, but provide a source of additional free surfactant which depends on the disassembly mechanisms of the aggregates [27] and allows for the maximum reduction in surface tension.

While many aspects of dynamic surfactant behavior have been detailed in theoretical works, there are relatively few experimental works [28,29] attempting to define and compare the properties of surfactants, fluorinated or otherwise. Exceptions to this are a few common low molecular weight surfactants, e.g. dodecyl sulfate, which have been well studied [30,31]. For dodecyl sulfate, a *meso*-equilibration is observed within 10 s for a given aqueous solution of 0.1 mol/L [27] and is too slow for many coating applications where millisecond ranges are needed [1–4].

The lack of significant experimental work on the dynamic properties of new surfactants can be explained through a number of reasons. First, the dynamic processes of surfactants occur quickly on very short time scales, which is inherently difficult to measure. The maximum bubble pressure tensiometry method has recently been successfully used to observe dynamic behavior at these short time scales. Second, interpretation of the dynamic results, especially to newcomers, is difficult given the number of overlapping processes, including aggregate disassembly, diffusion, adsorption and interfacial packing/orientation. Third, there is still much debate over the rate determining process behind dynamic surface tensions, and many different models exist to explain these phenomena [32]. Despite these difficulties, the dynamic properties of surfactants are still important for a large number of practical applications and should not be ignored.

Herein, we present the synthesis and characterization of a number of novel nonionic fluorosurfactants, particularly focusing on both static and dynamic properties. In all cases, multiple equally short R^F chains are attached to a branching core and then subsequently reacted with the hydrophilic group. Furthermore, structural effects of the nonionic hydrophilic groups, including size, polydispersity, and branching, are investigated. From these structures, the extent to which non-linear hydrophobic and hydrophilic groups influence the static and dynamic properties is addressed, and a basis for the future design of short-chain fluorosurfactants is developed.

2. Materials and methods

2.1. General procedures

The experimental details for the preparation and characterization of the nonionic hydrophilic-fluorophilic surfactants **6–8**, **9a–e**, **10**, **11** (Fig. 1), **18a** and **18b** (Fig. 3) are given in the supporting information. We recently described the synthesis of compounds **12a**, **12b**, **13**, **14a**, **14b** and **15–17** (Fig. 2) in a previous report

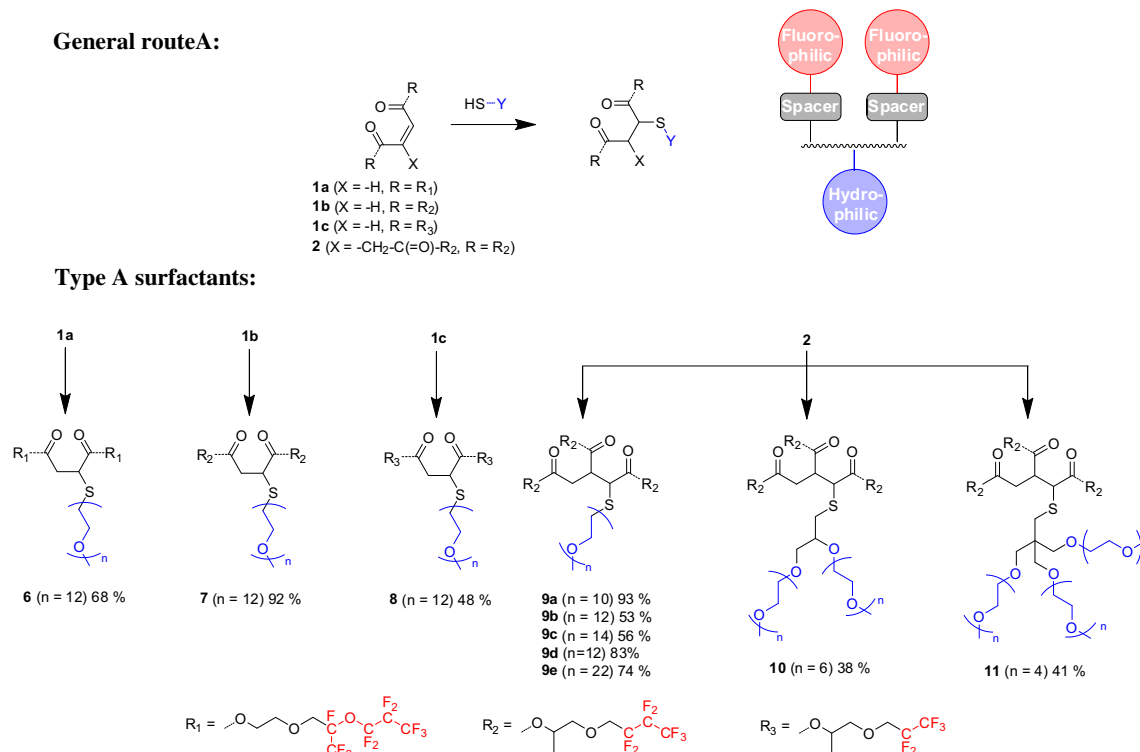


Fig. 1. Synthetic route A: Michael-addition of thiol-poly(ethylene glycol) monomethyl ether with maleic esters **1a–c** and aconitic ester **2**.

Download English Version:

<https://daneshyari.com/en/article/607231>

Download Persian Version:

<https://daneshyari.com/article/607231>

[Daneshyari.com](https://daneshyari.com)