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Synthesis and properties of hemifluorinated disodium alkanesulfonates

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ABSTRACT

Perfluorobutyl substituted disodium alkanesulfonates derivatives were synthesized and characterized as alternative substances to perfluorooctanesulfonic acid (PFOS, 1), a well-known surfactant. 1*H*,1*H*,2*H*,2*H*-nonafluorohexyl iodide, diethyl malonate and sultones were used to prepare disodium sulfonates 2 and 3 in three synthetic steps. The surface tension behavior of 2 and 3 were studied and critical micelle concentration values were noted to be 2025 mg/L and 2052 mg/L, respectively, at room temperature.

1. Introduction

Surfactants play major role as wetting, cleaning, foaming and emulsifying agents in many applications. The conventional surfactants usually contain one hydrophilic end and one hydrophobic group attached to it. These amphiphilic compounds are well known for their spectacular surface properties, which are dramatically influenced when attached to a perfluorocarbon chain as hydrophobic unit. Among which the manmade perfluorooctanesulfonic acid (PFOS, **1**) and its derivatives are proven to be most dependable substrates due to their special physicochemical properties [1,2]. It has a perfluorooctane chain as hydrophobic group and sulfonic acid as hydrophilic unit and show low surface tension as well as critical micelle concentration (CMC) values. PFOS and its derivatives have been used in stain repellents, coatings, plane hydraulic fluids, pharmaceuticals and electroplating, *etc.*, due to their heat, abrasion and chemical resistance [3,4]. Apart from all the advantages and uses of PFOS derivatives, they are listed under Stockholm convention on persistent organic pollutants (POPs) owing to their non-biodegradable wastage and toxic effects in the environment [5,6]. In recent years, efforts have been under progress to reduce the hazardous effects of PFOS derivatives by scientists and some industries all over the globe [7–10]. For instance, 3M company announced voluntary phase out of PFOS in 2000 and working on alternate surfactants that contain shorter C_4-perfluoro chain derivatives for less bio-accumulative, less toxic and sustainable substances [11–13].

On the other hand, it is proven that gemini surfactants which contain more than one hydrophobic as well as hydrophilic groups show significant effects on surface properties [14–16]. Our interest on making less fluorinated and efficient surfactants to understand their behavior by structural changes, has come up with a new design that partly meets the above-mentioned structural parameters. Thus, we have anticipated two surfactant structures (**2** and **3**) with two hydrophilic units that are sulfonic acids and one hemifluorinated hydrophobic tail as shown in Fig. 1.

The process of preparing PFOS related substances involves electrochemical perfluorination, telomerization of vinylidene fluoride or by controlled radical copolymerization of vinylidene fluoride and 3,3,3-trifluoropropene, *etc.* [9] In continuation of our efforts toward environmentally friendly PFOS alternatives for better surface properties [17], we here in present the synthesis and properties of perfluoroalkyl disulfonate class surfactants. Synthesis of such skeletons needed a simple route, where the introduction of perfluorinated alkyl chain must be easily accessible. However, the synthesis may not be cost-effective for some surfactants as they

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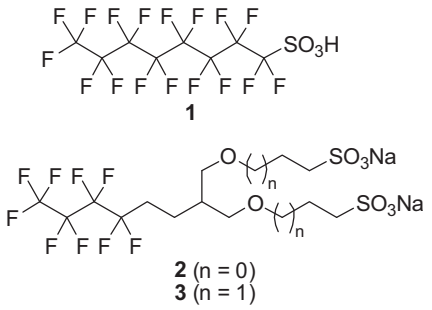


Fig. 1. Structures of PFOS and its proposed alternatives.

would be used as additives to conventional surfactants. As a preliminary study, the perfluorinated alkyl halide, 1*H*,1*H*,2*H*,2*H*-nonafluorohexyl iodide, **4** was used as fluorinated starting material to synthesize targeted sulfonic acid derivatives mentioned above in only three synthetic steps (Scheme 1). The other starting materials include diethyl malonate, 1,3-propanesultone and 1,4-butanesultone.

2. Results and discussion

To make difference from conventional, we report the synthesis of new hemifluorinated disodium alkanesulfonate compounds. The synthetic strategy involves a mono alkylation reaction of diethyl malonate (**5**) using alkyl halide **4** in the presence of sodium hydride in dry THF to afford **6** in 89% yield [18]. This reaction was conducted at various conditions (DMF, 0 °C to rt, 5 h, 68%; DME, 0 °C to reflux, 6 h, 56%; THF, 0 °C to rt, 5 h, 60%; THF, 0 °C to reflux 3 h, 89%) and standardized to ensure precise reaction yields of compound **6** in large amounts (50 g). Dibenzyl-malonate (**5a**) did not give any better results in increasing the yields instead decreased to 66% and thus avoided. The purity of compound **6** has found to be >97% by GC–MS. The ^{1}H NMR of **6** showed a multiplet for the single active proton of malonate around δ 3.44–3.40 ppm and corresponding carbon at δ 50.7 ppm in ^{13}C NMR, confirmed the product. The complete reduction of mono alkylated diethyl malonate **6** with lithium aluminum hydride smoothly afforded diol **7** in 91% yield, without affecting the perfluoroalkyl chain [19]. Further, this diol **7** was subjected to the nucleophilic ring opening of sultones in the presence of NaH as a base in THF. The propanesultone has given corresponding disodium sulfonate **2** in 86% yield and butanesultone has afforded disodium sulfonate **3** in 83% yield. All compounds are completely characterized by NMR (^{1}H, ^{13}C and ^{19}F), IR and mass spectral data. After the confirmation of structures and purity by analytical data, we move forward to the surface characteristics to evaluate the efficiency of these disodium alkanesulfonates in reducing the surface tension of water at the liquid–gas interface of their aqueous solution.

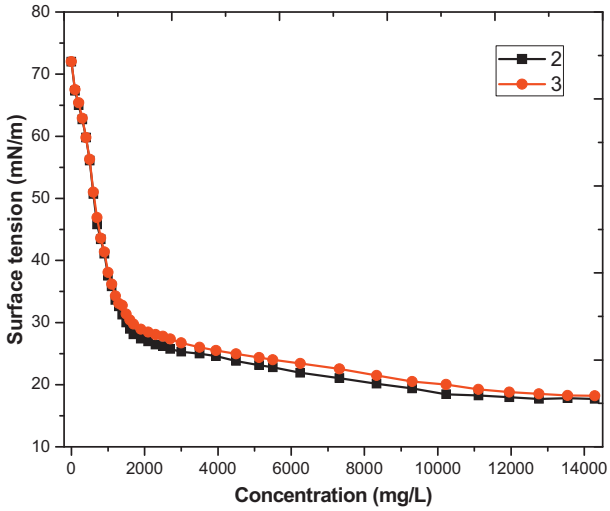
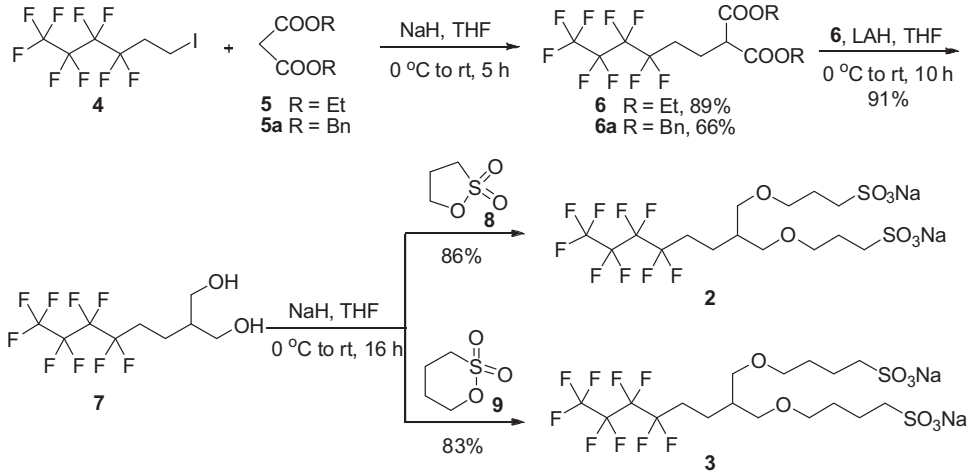


Fig. 2. Surface tension profiles of **2** and **3** in aqueous media.

Surface tension measurements of the two disodium sulfonates (**2** and **3**) were carried out using Wilhelmy plate tensiometer and a collective graph plotted between surface tension and concentration has been shown in Fig. 2. As the concentration increased, surface tension values were decreased. From the graph, it can be observed that compounds **2** and **3** have showed excellent surfactant activity as they decreased surface tension of water at low concentrations. The CMC values of the aqueous solutions of **2** and **3** were found to be 2025 mg/L and 2052 mg/L, respectively, at 25 °C, with the error of CMC less than 5% for both the compounds. The surface tension values of **2** and **3** are observed to be 26.0 mN/m and 27.4 mN/m, respectively, at their CMC values. Though there is



Scheme 1. Synthesis of hemifluorinated disodium alkanesulfonates **2** and **3**.