



## Fluorinated pyridinium and ammonium cationic surfactants



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### ABSTRACT

New classes of partially fluorinated cationic surfactants, including pyridinium sulfonates and ammonium hydrochlorides have been prepared in which a fluoroalkyl chain is interrupted either by ether oxygen ( $-\text{O}-$ ), or by methylene ( $-\text{CH}_2-$ ) units. These surfactants are obtained from multi-step syntheses via intermediate fluoroalkyl ethylene iodides ( $\text{RfO}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{I}$ ,  $\text{Rf} = \text{C}_3\text{F}_7$ ,  $\text{C}_2\text{F}_5$ ,  $n = 1-3$  or  $\text{Rf}(\text{CH}_2\text{CF}_2)_m(\text{CH}_2\text{CH}_2)_n$ ,  $\text{Rf} = \text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$ ,  $m = 0-2$ ,  $n = 1-2$ ) or fluoroalkyl iodides ( $\text{RfI}$ ,  $\text{Rf} = \text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3$ ,  $\text{C}_6\text{F}_{13}$ ). The surface activities of these fluorinated cationic surfactants were examined and compared to commercially available fluorinated cationic surfactants used as additives in oil field applications. Some examples demonstrated good performance relative to controls yet are more fluorine efficient because they have lower fluorine content than their perfluoroalkyl analogues. For the ammonium hydrochlorides, the effect of different spacer groups between the cation and the fluorinated chain including ethylene, butylene and isopropylidene on surface activity was also examined.

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## 1. Introduction

Fluorinated surfactants are a diverse class of surface activity agents. They have a wide variety of applications due to their unique properties such as surface tension reduction, wetting and leveling, exceptional stability in harsh environments (high temperature, high and low pH), hydro- and oleophobicity, etc. They are used as anti-blocking agents in architectural coatings, leveling and wetting agents in paints, inks and floor finishes, aqueous firefighting foams, hard surface cleaners, emulsifiers and dispersion aids for olefin polymerization, and additives in oil and gas extraction fluids [1–9].

In contrast to their hydrocarbon counterparts, fluorinated surfactants often exhibit significantly enhanced performance [8,10]. Hydrocarbon surfactants can generally reduce aqueous surface tension to ca. 30 dyn/cm, whereas surface tension reduction as low as 16 dyn/cm can be achieved with fluorosurfactants. Moreover, at the same performance level, the use rate of fluorosurfactants is much lower than that of hydrocarbon surfactants, 0.005–0.1 wt% versus 0.1–3 wt%, respectively. Fluorosurfactants possess outstanding stability in corrosive environments. Fluorosurfactants have been designed to perform

in organic, acidic and basic media, while hydrocarbon surfactants are limited to aqueous media. Furthermore the stability of the carbon fluorine bond also enables fluorosurfactants to deliver performance at high temperatures and high pressures.

Fluorinated surfactants are comprised of two key structural components, a hydro- and oleophobic perfluorinated carbon chain (e.g.,  $\text{F}(\text{CF}_2)_n^-$ ), a hydrophilic group, and optionally a spacer separating these two groups. In fluorinated cationic surfactants, the cation is typically a quaternary ammonium group or a protonated amine, including heterocycles [8]. Fluorinated cationic surfactants can be highly effective surface tension reducing and foaming agents in acidic and salt environments. Also, because they are positively charged they can be used to modify negatively charged surfaces. For example, textile surfaces can be modified with fluorinated cationic surfactants to reduce fiber–fiber, fiber–metal, and fiber–ceramic coefficients of friction [11]. Fluorinated cationic surfactants are additives in aqueous firefighting foams to improve foaming and formulation drainage [8]. They also give improved yields in the emulsion polymerization of olefins [12]. In the case of oil field applications, the oil and gas extraction is conducted in a high temperature, high corrosion environment, and fluorinated cationic surfactants function well in these extraction fluids due to their outstanding thermal and chemical stability [9,13]. In this application, the positively charged surfactant electrostatically absorbs to negatively charged surfaces such as

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rock fines and sand proppant to reduce capillary forces and improve the recovery of hydrocarbons (oil/gas) and/or the stimulation fluid used to open up the formation. In addition, the cationic surfactant inhibits corrosion by forming a protective film on the metal parts of the well [14].

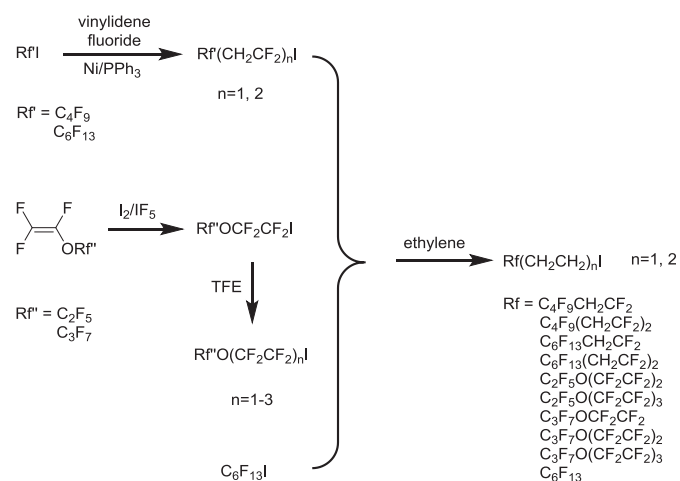
Fluorinated surfactants are usually more expensive than hydrocarbon surfactants. Although their unique performance attributes offset the added cost to some degree, it is also desirable to increase the fluorine efficiency; i.e., boost the performance of the surfactant so that lesser amounts of the expensive fluoro-surfactant are required to achieve the same or better level of performance. It is thus desirable to reduce the chain length of the perfluoroalkyl groups or to reduce the amount of fluorine within a partially fluorinated group, thereby reducing the total fluorine present while still achieving the same or superior surface effects. Additionally, alternative fluorinated materials, including surfactants, with improved environmental properties have been the subject of significant recent attention and review [15–22].

We describe here the syntheses of a few novel fluorinated pyridinium sulfonates and fluorinated ammonium chlorides in which the fluorinated carbon chains are interrupted either by methylene ( $-\text{CH}_2-$ ) or ether (e.g.,  $-\text{O}-$ ) linkages. We further show that in comparison to their perfluorinated analogues, these interrupted structures are more fluorine efficient with respect to their surface-active properties. Such a design allows these surfactants to maintain the chemical stability required for harsh application environments, while also translating into reduced cost.

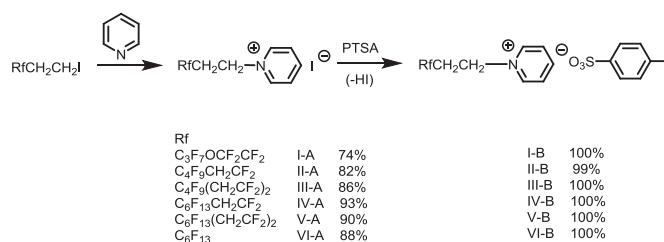
## 2. Results and discussion

### 2.1. Synthesis of fluoroalkyl ethylene iodides

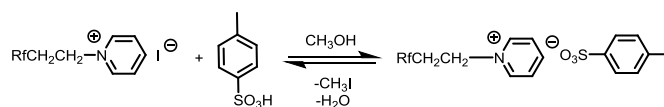
The fluoroalkyl ethylene iodide synthesis is shown in Scheme 1 [23,24]. In the case of fluoroalkyl chains interrupted with methylene groups, the thermal or redox-initiated insertion of vinylidene fluoride (VDF) into fluoroalkyl iodide bonds has been studied extensively by Ameduri and others [25–29]. Here a metal-mediated vinylidene fluoride insertion of fluoroiodide, followed by radical-mediated ethylene insertion is employed [24]. Access to the fluorinated ethers was accomplished by reaction of perfluoro-vinyl ether with  $\text{I}_2$  and  $\text{IF}_5$  to give the fluorinated ether iodides [24], subsequent thermal telomerization with tetrafluoroethylene to extend the chain length, and then insertion of one equivalent of ethylene. The example of a double ethylene insertion in the case of  $\text{C}_6\text{F}_{13}(\text{CH}_2\text{CH}_2)_2\text{I}$  was achieved by reaction of  $\text{C}_6\text{F}_{13}\text{I}$  and ethylene in



Scheme 1. Synthesis of fluoroalkyl ethylene iodides.



Scheme 2. Synthesis of fluorinated pyridinium surfactants.



Scheme 3. Reaction of fluorinated pyridinium iodides with *p*-toluene sulfonic acid.

the presence of radical initiator [30]. Fractional distillation was applied in each step for material purification.

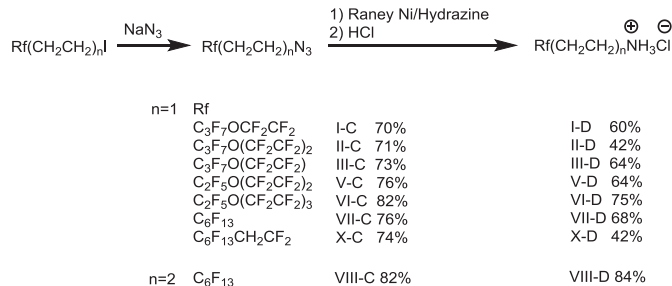
### 2.2. Synthesis of fluorinated pyridinium surfactants

The fluoroalkyl ethylene iodides were heated with pyridine at  $80^\circ\text{C}$  for 20 h (Scheme 2). The resulting pyridinium iodide was filtered, washed with ethyl acetate, and dried in the vacuum oven overnight. Yields range from 70 to 95%. Treating this intermediate with *p*-toluene sulfonic acid in methanol at  $70^\circ\text{C}$  for 24–48 h offered the final product in quantitative yields. In this step methyl iodide and water are generated and constantly removed by distillation to drive the reaction to completion (Scheme 3). These reactions are conveniently followed by periodic gas chromatography of the distillate to monitor the methyl iodide removal. In addition to driving the equilibrium to products, the water stripping may be important to prevent leveling of the acid catalyst and potential inhibition of the reaction rate.

The above fluorinated pyridinium salts were subjected to performance tests as 50 wt% solutions in methanol.

### 2.3. Synthesis of fluorinated ammonium surfactants

Fluoroalkyl azides with an ethylene spacer were prepared in moderate yields by the biphasic reaction of fluoroalkyl ethylene iodides and sodium azide in the presence tetrabutylammonium bromide as phase transfer catalyst at  $100^\circ\text{C}$ . Raney nickel and hydrazine reduction of the azide intermediates was used to generate the free amines, followed by acidification with HCl to provide the fluoroalkyl ammonium chlorides (Scheme 4).



Scheme 4. Synthesis of fluorinated ethylene ammonium surfactants.

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