# The New Fluorocarbon- Hydrocarbon Unsymmetrical Bolaform Surfactant: A Novel Anti-Foaming Agent

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## Abstract

We report the interfacial properties of a new fluorocarbon-hydrocarbon hybrid surfactant $[OH(CH_2)_{11}N^+(C_2H_4)_2(CH_2)_2(CF_2)_5CF_3$ $I^-$, or FHUB], which has a fluorocarbon chain as well as a w-hydroxyalkyl chain. This new hybrid surfactant has properties that are different than classical hydrocarbon- and fluorocarbon-containing surfactants. This difference is created by combining a fluorocarbon chain and the hydrocarbon chain in a way to give the best performance (i.e., low critical micellization concentration, low limiting surface tension, salt insensitivity, low foaming ability). The unsymmetrical bolaform character of FHUB gives rise to the salt-insensitive interfacial behavior and low foaming ability of this surfactant. The presence of the fluorocarbon chain reduces the critical micelle concentrations of this new hybrid surfactant to a lower value (0.5 mM in 100 mM LiBr) compared to classical ionic and unsymmetrical bolaform surfactants such as dodecyltrimethylammonium bromide (2.5 mM in 100 mM LiBr) and HTAB, w-hydroxyundecyltrimethylammonium bromide (21 mM in 100 mM LiBr). Moreover, the presence of the more rigid hydrophobic part (fluorocarbon chain) affects the aggregation properties of FHUB. The FHUB molecules start to form aggregates with less curvature at a low surfactant concentration. The formation of small aggregates, which have been reported to form by unsymmetrical bolaform surfactants, is prevented. As a result, the limiting surface tension of FHUB is obtained as a low value. In addition to these properties of FHUB, it has been determined that this new surfactant is able to break foams within seconds even at low surfactant concentrations (c < 0.3 mM).

## Introduction

Fluorocarbons are characterized by their exceptional chemical and biological inertness, extreme hydrophobicity, lipophobicity, high gas-dissolving capacities, low surface tensions, high fluidity and spreading coefficients.[1, 2] These unique properties of fluorocarbons are the basis of applications such as biomedical applications.[3,4] Although there are several advantages of fluorinated surfactants over hydrocarbon surfactants, their limited solubility in aqueous solutions and limited mixing ability with organic materials (even when used with hydrocarbon surfactants they tend to phase separate macroscopically or microscopically) limit the use of fluorinated surfactants in several processes.[5] There are several studies present in which hybrid surfactants (i.e., surfactants having fluorinated and hydrogenated parts) were designed.[6-9]

Recently, a detailed investigation of a hybrid anionic surfactant sodium 1-oxo-1-[4-(fluoroalkyl)phenyl]-2-alka-nesulfonates ($FC_m$-$HC_n$ : (m, n) in which m and n are (6, 4), (6, 2),and (4, 6)) has been reported.[8,9] From this study it is concluded that an increase in the fluorocarbon chain length of a hybrid surfactant gave rise to an increase at the Krafft temperature and a decrease at the cmc and limiting surface tension.[8] The aggregation number of a $FC_m$-$HC_n$ micelle was determined to be smaller than those of typical ionic hydrocarbon surfactants.[9] The value of area per molecule for $FC_m$-$HC_n$ was obtained as 81-122 $\text{Å}^2$/molecule.[9,10] It has been further demonstrated that a concentrated aqueous solution of $FC_6$-$HC_4$ exhibits unusual viscoelastic behavior.[11] The necessary condition to exhibit thermoresponsive viscoelastic behavior was suggested as having a hybrid structure.[11]

Unsymmetrical bolaform surfactants have been introduced for active[12-15] and passive control[16-18] of surface and bulk properties of aqueous solutions recently. In terms of active control of bulk and solution properties, the electrochemical control of the oxidation state of redox-active ferrocene group within the structure of $Fc(CH_2)_{11}N^+(CH_3)_3Br^-$, which have been shown to behave like unsymmetrical bolaform surfactant, leads to large and reversible change in surface tension and aggregation state of the aqueous solution.[12,13] It is demonstrated that, the presence of a hydrophilic group at the $\omega$ position within the surfactant structure affects the molecular forces acting on the system, which results in different bulk and surface properties of this class of surfactants compared to classical ionic surfactants.[16] The principal conclusions to emerge from past experimental and theoretical studies of these types of surfactants are (i) surfactants tend to occupy larger areas at the interface than classical ionic surfactants such as DTAB and SDS, (ii) they adopt a looped configuration at the interface, (iii) their limiting surface tensions are relatively high, (iv) their cmc values are higher than those of the classical ionic surfactants which have the similar hydrophobic driving force for adsorption, (v) the dominant contribution at surface tension lowering is the configurational term, not the electrostatic as expected from an ionic surfactant, (vi) they are less sensitive to variations in the ionic strength of the aqueous subphase compare to classical ionic surfactants, and (vii) their abiliy to form foam is low.[12-18]

The control or elimination of the foam that arises in many industrial processes can be the crucial factor promoting smooth plant operation. Indeed, many of the concepts of colloidal stabilization, such as the importance of double layer, steric and van der Waals interaction, operate in foams. Electrically charged species at the lamella surface exert a repulsive force on the corresponding charged species on the opposite lamella surface this effect opposes lamella drainage and thus is a foam stabilizing factor.

In this paper, we present the interfacial and bulk behavior of the new fluorocarbon-hydrocarbon hybrid unsymmetrical bolaform surfactant (FHUB) $(OH(CH_2)_{11}N^+(C_2H_4)_2(CH_2)_2(CF_2)_5CF_3$ $I^-$ see Figure 1). The structure of this

surfactant is designed on the basis of the previous observations of fluorocarbon surfactants, hybrid ionic surfactants and unsymmetrical bolaform surfactants. In the scope of this study, it is planned to combine several features of fluorocarbon surfactants[15-18] and unsymmetrical bolaform surfactants[16] into the structure of this new molecule. The proposed configuration of the FHUB molecules within air/water interface has been shown in Figure 2. Like the HTAB molecules, the presence of the hydroxyl group at the other end of hydrocarbon chain is expected to result in changes in its configuration (looped configuration). For that reason, it is also expected from FHUB to not form stable foam.



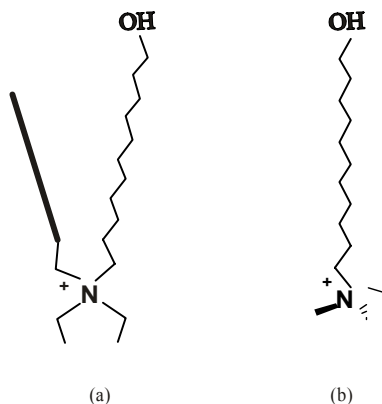(a)                              (b)

Figure 1. Molecular structures of the new fluorocarbon hydrocarbon unsymmetrical bolaform surfactant FHUB (a) and the unsymmetrical bolaform surfactant HTAB (b)
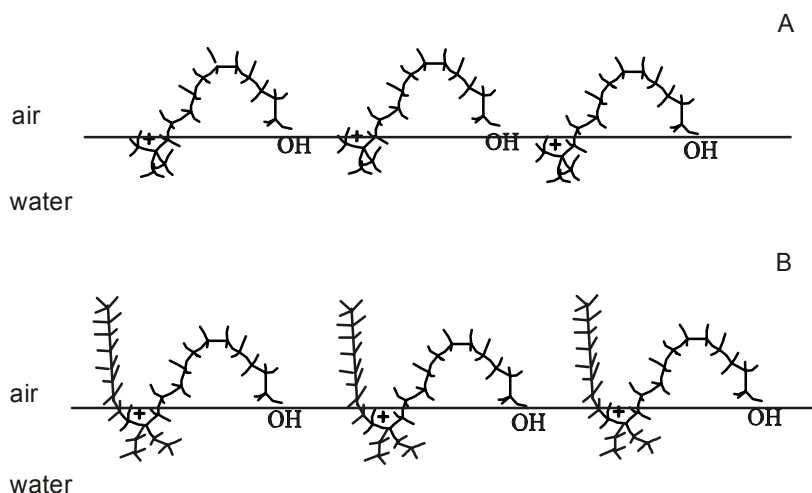


Figure 2. Schematic illustration of likely conformation of (A) HTAB and (B) FHUB

**Materials and Methods**

1,1,1,2,2,3,3,4,4,5,5,6,6,-Tridecafluoro-8-iodooctane, 11-bromo-1-undecanol, diethyl amine, trimethylamine, 11-bromoundecane and DTAB were purchased from Across (Belgium). The acetone, hexane, diethyl ether and lithium bromide were purchased from Sigma (Germany). The hybrid surfactant (11-

hydroxundecyl) tridecafluorooctane diethylammonium iodide ($OH(CH_2)_{11}N^+(C_2H_4)_2(CH_2)_2(CF_2)_5CF_3I^-$ or FHUB) was synthesized in our laboratory as described elsewhere.[19]

Aqueous surfactant solutions were prepared freshly for each experiment using water from a water purification system (Barnstead, U.S.A.). The equilibrium surface tensions of aqueous solutions of FHUB were measured using a wilhelmy plate method in a tensiometer (Kruss, Germany). All surface tension measurements were repeated at least twice. All the glassware was cleaned in piranha solution (18 M $H_2SO_4$, 30 % $H_2O_2$, 70:30 v/v) The Krafft temperature of FHUB in water was measured as 38°C. Because FHUB has the Krafft temperature higher than room temperature, all surface tension measurements were performed at 40°C. Surface tension measurements were performed in 1mM and 100 mM LiBr electrolyte at pH 2.

Measurements of quasi-elastic light scattering were done in order to determine the hydrodynamic radii of the aggregates. Quasi-static light scattering experiments were performed using a Malvern Zetasizer-1000 with a 50 mW 532 nm laser (Malvern, UK). Aqueous solutions were prepared using water filtered through a 0.22 $\mu$m filter. The samples were centrifuged for 1 hr and allowed to equilibrate at 40°C for 20 min before the measurements. Measurements were repeated two hours and 10 hours after preparation. No increase in the size of aggregates is determined. The angle of the detector was set at 90°. UV-vis absorption spectra were recorded on a UV-vis spectroscopy (Hitachi 150-20 spectroscopy). All the measurements are done at 40°C. For the solubilization experiments excess amount of water insoluble dye (indigo) added to aqueous surfactant solutions. Solutions are mixed over 24 h at 40°C. Prior to measurements, surfactant solutions are either centrifuged or filtered to remove dispersed dye particles within the aqueous solution.

A conventional cylinder shake testwasused to evaluate the foaming performance of surfactant/antifoam mixtures. Foaming experiments were carried out in 100 mL volumetric cylinders using 15 mL of the foaming solution. The stoppered cylinder was shaken by hand 10 times, and the foam height was measured immediately (within 10 s) after cessation of shaking.

**Results and Discussion**

Figure 3 shows measurements of the equilibrium surface tensions of aqueous solutions of FHUB that contain either 1 or 100 mM LiBr electrolyte. Inspection of Figure 3 reveals that each plot of the surface tension displays a sharp break corresponding to the onset of aggregation in the bulk solution. The surface tension reduction obtained from FHUB are 25 and 29 mN/m for solution containing 100 and 1 mM LiBr electrolyte, respectively. The cac's of FHUB are determined as 0.50 and 0.45 mM for 100 and 1 mM LiBr, respectively.
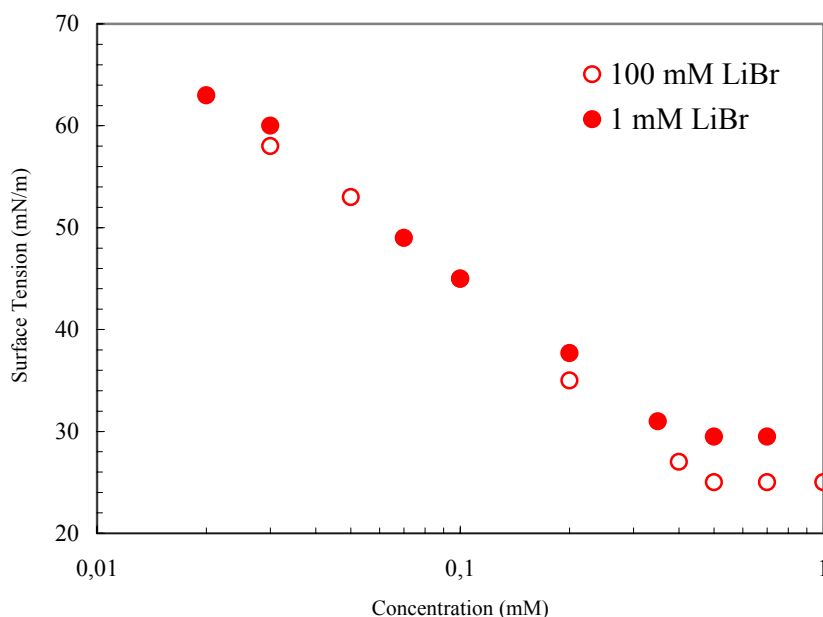
Figure 3. Surface tension of aqueous FHUB solutions (○) 100 mM LiBr, (●) 1 mM LiBr.

The summary of the properties of FHUB as well as the comparison to several surfactants are given in Table 1. The chemical structure of FHUB (see Figure 1) resembles to the dimeric cationic surfactant DDAB (didodecyldimethylammonium bromide). Unlike DDAB, FHUB bears a fluorocarbon chain. The hydrophobic free energy contribution ($g_{hyd}$) of a fluorocarbon chain to the free energy of the monolayer is reported to be larger that of a hydrocarbon chain having the same number of carbon.[20] This high hydrophobicity of the fluorocarbon chain gives rise to the formation of a denser monolayer and formation of aggregates at a lower surfactant concentration.[20] The hydrophobic driving forces for adsorption ($g_{hyd}$) of FHUB and DDAB are calculated by using the formulations that have been shown previously to be successful in predicting $g_{hyd}$ of surfactants.[20] The hydrophobic free energy contribution to the free energy of the monolayer of FHUB is calculated as −34.4 kT, which is larger than the $g_{hyd}$ of DDAB (Table 1). This difference suggests that the FHUB should start aggregation at a lower concentration than DDAB. However, the experimentally determined cmc of FHUB is larger than the cmc of DDAB. The second difference in the structure of FHUB compared to that of DDAB other than the presence of the fluorocarbon chain is the presence of the hydroxyl group at the other end of the hydrocarbon chain. The hydroxyl group at the end of the hydrocarbon chain acts as hydrophilic group when the carbon number of the hydrocarbon chain is less than 12.[20] Because one end of the hydrocarbon chain of FHUB is tethered by the ionic head group, the hydrophilicity of OH group gives rise to the looped configuration to the hydrocarbon chain.[16] Previously, it has been revealed that the surface tension reduction mechanism of unsymmetrical bolaform surfactants was shown to be dominated by the

configurational constraints and not the electrostatic interactions, as expected from a classical ionic surfactant like DTAB.[5] This configurational constraints of FHUB prevent the adsorption of surfactant to the interface and prevent the formation of aggregates at a low surfactant concentration. In other words, the cmc of FHUB is larger than that of DDAB because of the differences at their configuration at the air-water interface even though the hydrophobic free energy (which favors micellization) of FHUB is larger than that of DDAB.

Table 1. Comparison of interfacial and bulk properties of FHUB with other types of surfactants

| Surfactant | CMC (mM) | $\gamma_{lim}$ (mN/m) | $A_{lim}(\text{Å}^2)$ | $g_{hyd}$ (kT) | $T_{Krafft}$ (°C) | Reference. |
|---|---|---|---|---|---|---|
| FHUB[a] | 0.450 | 25 | 88±5 | -34.4 | 38 | |
| DDAB[b] | 0.014 | 19 | 103 | -32.0 | <25 | 22 |
| HTAB[a] | 21.000 | 48 | 68±5 | -16.0 | 28 | 16 |
| DTAB[a] | 2.500 | 37 | 41±5 | -18.5 | <0 | 10 |
| $FC_mC_n^c$ (m=6) | 0.045 | 22 | 100±5 | -37.8 | 26 | 21 |

[a] in the presence of 100 mM LiBr at 40°C
[b] in water at 25°C
[c] anionic hybrid surfactant in water at 25°C (see reference 21)

The limiting area per FHUB molecule at the interface is determined by using the Gibbs adsorption equation.[9,10] At the presence of 100 mM LiBr, the minimum area per molecule of FHUB is determined to be 88 ± 5 $\text{Å}^2$/molecule, which is larger than the minimum area of a classical ionic surfactant (DTAB) and smaller than the minimum area of a cationic dimeric surfactant (DDAB). Because FHUB, DTAB and DDAB bears one ionic headgroup, this difference at the area per molecules is caused by differences in the configuration of surfactants at the interface. Moreover, the minimum area per FHUB molecule within the interface is larger than the minimum area per molecule of HTAB but smaller than the minimum area per molecule of DDAB, which can be explained simply by the presence of the fluorocarbon chain.

One of the properties which distinguishes the unsymmetrical bolaform surfactants from the classical ionic surfactants is their salt-insensitive interfacial behavior.[16] This behavior is related to the dominant contribution to the lowering of the surface tension.[16] The effect of the electrolyte concentration on the behavior of FHUB is summarized in Table 2. It has been revealed from Figure 3 that at a low surfactant concentration region (C < 0.1 mM) the surface activity of FHUB is not affected by the change in the electrolyte concentration. However, at a higher surfactant concentration (0.1 < C < 0.45), the effect of electrolyte concentration on the surface activity is observed. It is known that addition of the electrolyte to the solution of a classical ionic surfactant results in screening of the electrostatic repulsions between surfactant molecules. As a result, a decrease at the cmc is

observed. The cmc of HTAB, on the other hand, is demonstrated to be less sensitive to changes in the electrolyte concentration than classical ionic surfactants (Table 2). The FHUB molecule is proposed to behave like an unsymmetrical bolaform surfactant. The minimum area per FHUB molecule, which is calculated as 88 $Å^2$/molecule in the presence of 100 mM LiBr, indicates the unsymmetrical bolaform structure of that molecule. Because the area per molecule of FHUB is larger than that of HTAB in the presence of 100 mM LiBr, the electrostatic interactions between FHUB molecules are expected to be smaller than those of HTAB, which further reduces the effect of the electrolyte concentrations on the interfacial behavior of FHUB. In parallel to our expectations the cmc of FHUB is determined to be less sensitive to change in electrolyte concentrations, as is seen from Table 2. The addition of salt in this case causes the slight increase in the cmc of FHUB. This unexpected behavior of FHUB is proposed to be related to the different aggregate properties of FHUB at 1 and 100 mM LiBr. The limiting surface tension of FHUB, however, shows a decrease as a result of the addition of electrolyte. This change in the limiting surface tension of FHUB with the addition of electrolyte is the largest compared to those of DTAB and HTAB. As mentioned before, the limiting surface tension of a surfactant solution is actually determined by the concentration in which aggregates are starting to form. The cmc of FHUB is determined to increase by the addition of electrolyte. The increase of the cmc`s and the decrease of the limiting surface tensions of FHUB solutions with increase at electrolyte concentration are hypothesized result from the differences in the aggregation states of FHUB compared to those of DTAB and HTAB.

Table 2. Effect of electrolyte concentration on surface activity and aggregate size of FHUB, classical ionic and unsymmetrical bolaform surfactants (T= 40°C, pH=2)

| Surfactant | CMC (mM) | | $\gamma_{lim}$ (mN/m) | | $D_h$ (nm) | |
| --- | --- | --- | --- | --- | --- | --- |
| | 1 mM LiBr | 100 mM LiBr | 1 mM LiBr | 100 mM LiBr | 1 mM LiBr | 100 mM LiBr |
| FHUB | 0.4 | 0.45 | 29.0 | 25.0 | 65±5 258±20 | 388±20 |
| HTAB | 29.0 | 21.0 | 47.0 | 47.0 | <1 | <1 |
| DTAB | 11.0 | 2.5 | 36.0 | 35.5 | 3±1 | 3±1 |

The bulk properties of unsymmetrical bolaform surfactants are reported to be different than those of the classical ionic surfactants.[25] For example, HTAB molecules are demonstrated to form small aggregates with a small aggregation number.[25] The fluorocarbon chain of FHUB is hypothesized to make the formation of small aggregates harder as a result of the more rigid structure of a fluorocarbon chain, which makes the formation of aggregates with high curvature (small aggregates) less possible. To evaluate this hypothesis, the sizes of the aggregates formed by FHUB are determined using quasi-elastic light scattering. The hydrodynamic diameters of FHUB, HTAB, and DTAB are reported in Table

2. The aggregate size of a classical ionic surfactant such as DTAB is determined to form globular micelles. The instrument that we used in this study was not able to detect the aggregates of HTAB ($D_h$<1 nm). The aggregate size of FHUB is expectedd to be different than those of the aggregates of DTAB and HTAB. First, FHUB forms aggregates which are larger in size with less curvature which is parallel to our expectations from the fluorocarbon containing surfactant. Second, the change in the electrolyte concentration from 100 to 1 mM LiBr gives rise to transition in the aggregate size, as seen from Table 2. At low electrolyte concentrations (1 mM LiBr), aggregates with 65 and 250 nm diameter coexist. When the electrolyte concentration is raised to 100 mM, aggregates with a diameter of 388 nm are formed. In a previous study, aggregates formed by a fluorocarbon-hydrocarbon hybrid anionic surfactant are reported to have interesting thermo-responsive behavior which is explained by the change in the aggregate properties.[21] When the aggregates have been investigated in detail, it has been observed that close to the cmc (~0.5 wt%) small spherical aggregates with aggregation number of ~22 are present.[23] An increase at the surfactant concentration from 2 to 10% results in the formation of larger aggregates. In the 10 % solution, rodlike micelles and multilayer vesicles (~500 nm in diameter) have been determined.[23] Moreover, the anionic hybrid surfactant has been reported to show a transition in the aggregate size as a result of the increase in the temperature from large aggregates with a 500 nm diameter to a state in which small and large spherical aggregates coexist.[24] A further increase in the temperature results in the formation of small aggregates (80 nm).[24] Within these large aggregates, the hydrocarbon and fluorocarbon rich region is self organized. However, when the electrolyte concentration is decreased at the same temperature or the temperature is increased at the same electrolyte solution, aggregates with smaller size are a favored and mix of large and small aggregates is determined.  To characterize the bulk properties of FHUB to identify the similarities and differences with anionic hybrid surfactants the effects of the surfactant concentration and the temperature on aggregate size are further investigated.

The aggregate size of FHUB, which is determined close to cmc (1 mM), is measured as 323±20 nm by light scattering (Figure 5). Although FHUB is a hybrid surfactant, the configuration of FHUB within the aggregate is expected to be different than the anionic hybrid surfactant. The presence of ω-OH group constrains the configuration of the hydrocarbon group (looped configuration). The combination of the looped configuration of the hydrocarbon chain with the presence of the fluorocarbon chain is expected to prevent the formation of small aggregates. The formation of large aggregates even at a low surfactant concentration is evaluated as the indication of differences in the aggregation state or the differences at the configuration of surfactants that is adapted within the aggregate of FHUB and anionic hybrid surfactant. An increase at the surfactant concentration from 1 to 3 mM leads to the formation of larger aggregates with a 388±20 nm diameter (Figure 5). The further increase in the surfactant concentration to 5 mM result in the formation of smaller aggregates

with a 234±20 nm diameter.  This maximum could be the indication of a change in the aggregate type of the surfactant. The aggregate geometry of this new surfactant is still under investigation; to give a better understanding and better comparison, the temperature dependent change at aggregate sizes below and after the maximum point needs to be examined.
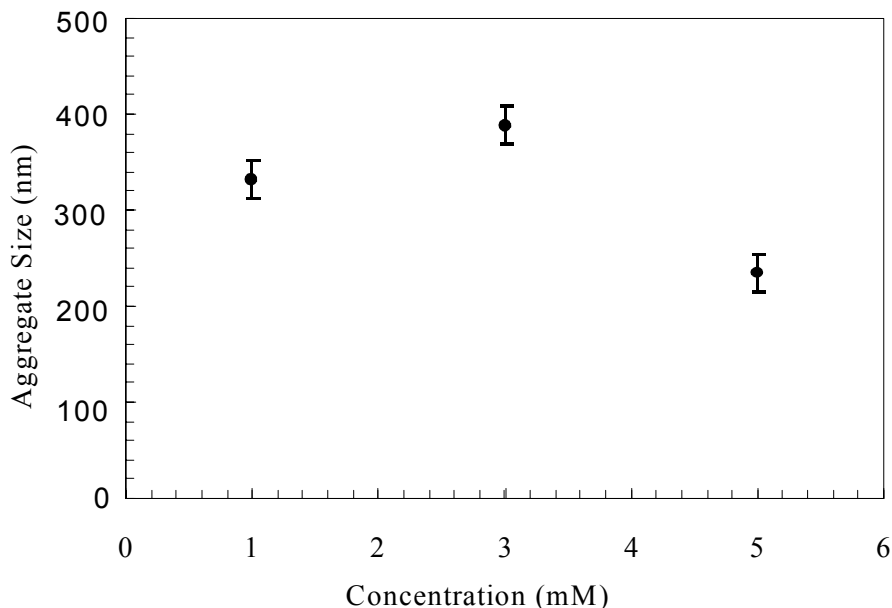


Figure 5. Effect of FHUB concentration on the aggregate size (100 mM LiBr, 40 °C at pH 2)

The impact of FHUB and SDS after their cmc's on the foaminess was assessed using a simple shake test. The initial foam height was measured within seconds after cessation of shaking, allowing only enough time for determination of the foam height. It is determined that a classical ionic surfactant SDS forms foam approximately 6 cm height. The most iportant, this foam is stable over an hour. On the other hand FHUB (above it's cmc) forms 0.5 cm foam which disappears instantly. Moreover addition of 0.01 mM FHUB in to the 3 mM SDS solution results in the decrease at the foam stabilty and addition of 0.05 mM FHUB both reduces the foam height down to 2.5 cm and foam stability signifcantly (foam diappears within 10 min).

**Conclusions**

In this study, we demonstrated the surface and bulk behavior of a new fluorocarbon/hydrocarbon hybrid unsymmetrical bolaform surfactant. This surfactant combines the properties of unsymmetrical bolaform surfactants and fluorocarbon hydrocarbon hybrid surfactants into one molecule. Although this molecule has a cationic headgroup, its surface properties were demonstrated to

be insensitive to change in the electrolyte concentration. This salt insensitive behavior of FHUB is demonstrated to be related to its unsymmetrical bolaform structure. Unlike the unsymmetrical bolaform surfactant, FHUB was able to form aggregates at lower concentrations than classical ionic surfactants. This behavior was simply related with the presence of fluorocarbon chain, which is more hydrophobic than the hydrocarbon chain. The other function of the fluorocarbon chain within the structure of FHUB was to prevent to formation of small aggregates so that the surface tension of the surfactant solution will continue to decrease. This new surfactant was able to reduce surface tension to a value which is lower than the limiting surface tension of the classical ionic surfactant DTAB (25 mN/m vs. 35 mN/m). The aggregation behavior of FHUB was determined to be different than the hybrid anionic surfactants. This new surfactant was able to form large aggregates with less curvature. Due to its configuation in the air-water interface FHUB does not result in the foam formation. Studies on this subject are still continuing by focusing on the dynamics of foam formation.

## Acknowledment

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