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SURFACTANTS DERIVED FROM 2-HYDROXY-4-(METHYLTHIO)BUTYRIC ACID: PHASE BEHAVIOR, INTERFACIAL ACTIVITY, MICROEMULSIONS AND MORE

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SURFACTANTS DERIVED FROM 2-HYDROXY-4-(METHYLTHIO)BUTYRIC ACID: PHASE BEHAVIOR, INTERFACIAL ACTIVITY, MICROEMULSIONS AND MORE

A DISSERTATION APPROVED FOR THE
DEPARTMENT OF ENGINEERING

BY

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This dissertation is dedicated to my family and friends, especially to my parents:

Jiashu Dong and Aiping Yu

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Abstract

Surfactants derived from 2-hydroxy-4-(methylthio) butyric acid were investigated. Anionic surfactants derived from this molecule have excellent water solubility, hardness tolerance and surface activity. Nonionic surfactants based on this molecule presented excellent phase behavior in water, high surface activity, good foaming/wetting ability, and good laundry performance. The headgroup hydrophilicity of the nonionic surfactants were enhanced with oligomeric sulfoxide ester units or extra ethylene oxide units, and their water solubility and surface activity were improved from the monomer sulfoxide esters, while maintaining good foaming, wetting and laundry performances. The application of these surfactant classes was further explored; a potential foam-breaker class and a promising emulsifier family were found.

Chapter 1 Introductions

1.1 Surfactants

Surfactants have been known for thousands of years. From soaps to novel products such as alkylbenzene sulfonates and alkyl poly-glucosides, surfactants are interface-altering compounds for liquids, typically water, which act at low concentrations. The structure of a surfactant contains at least one lyophilic (solvent liking) and one lyophobic (solvent hating) groups, to drive interfacial adsorption. In most cases, surfactants are made of one hydrophilic "headgroup" and one hydrophobic "tailgroup". Based on the nature of the headgroups, surfactants are classified as anionic (- charge), cationic (+ charge), zwitterionic (both charges) and nonionic (no charge).

In this dissertation, surfactant structures derived from a water soluble molecule 2-hydroxy-4-(methylthio)butyric acid (see Figure 1-1) are discussed. Based on various synthetic strategies, anionic surfactants, nonionic surfactants and nonionic surfactants with enhanced amphiphilicity were produced, their performances were characterized, and their applications were explored.

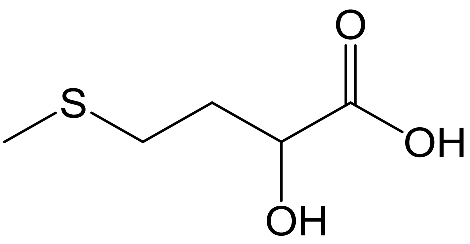


Figure 1-1 Schematic structure of 2-hydroxy-4-(methylthio) butyric acid

1.1.1 Anionic surfactants

Anionic surfactants with carboxylate moieties have been used for thousands of years; soap was first made from the hydrolysis of naturally-occurring oils/fats. Fatty-acid surfactants have an excellent combination of properties including low critical micelle concentration (CMC), low surface tension at the CMC, good foaming characteristics, and mildness when applied to skin. However, the 20th century has seen the use of these surfactants relative to other anionic surfactants decrease significantly for many reasons. From a property perspective, the most significant disadvantage of these surfactants is their propensity for precipitating when divalent cations are present, e.g., calcium and magnesium (hardness tolerance).

One well-known strategy to increase the hardness tolerance of anionic surfactants is to add branches to the linear main chain.[1] However, early attempts to produce hardness tolerant soaps such as highly-branched alkylbenzene sulfonates made from polypropylene failed because of its poor biodegradability.[2] People then started to examine less recalcitrant branching in the surfactants, for example, a lower degree of branching in the hydrophobic group.[1a] Another synthetic strategy to produce branched carboxylic acid molecules is to use a head group with multiple hydrophilic moieties. As presented in Figure 1-1, 2-hydroxy-4-(methylthio)butyric acid has the potential to combine both the aforementioned structural aspects in one molecule. This molecule contains both hydroxyl functionality and carboxylic acid functionality where there is a sulfur-containing branch between the two. This particular compound is produced commercially in large quantities because it can convert into L-methionine in animal liver and is used extensively in animal feed.[3] By esterifying the alcohol and neutralizing the acid group, a branched carboxylic acid surfactant was generated. The branching in this molecule should be considered biodegradable, because of the absence of secondary/tertiary carbons which caused the recalcitrance of highly branched hydrophobes. Further, the ester linkage is easily broken via hydrolysis.

In Chapter 3, three anionic surfactants synthesized from 2-hydroxy-4-(methylthio) butyric acid are investigated. Their structures were characterized with high performance liquid chromatography (HPLC). Their properties as surfactants, such as water solubility, CMC, surface tension at CMC (γ_{CMC}), Krafft temperature, calcium tolerance, foaming ability and wetting performance were studied and compared with anionic surfactants with similar structures. The effect of the branching and sulfoxide group of the molecules in their performance as a surfactant is explored by comparing the results to alkylcarboxylate salts.

1.1.2 Nonionic surfactants

Nonionic surfactants are widely formulated into household, personal care and industrial products. Alkyl-phenol ethoxylates, the majority being nonyl-phenol ethoxylates (NPEs), are a common type of nonionic surfactant. NPE surfactants have low CMC, low surface tension and high feedstock availability. In 2000, NPEs dominated the nonionic surfactant market with a 45% share.[4] However, NPE formulation has been and will keep decreasing because of its potential environmental issues. Researchers claim that potential hormone disruptors, namely estradiol analogues, occur during degradation of NPEs.[5] In 2010, the US Environmental Protection Agency announced their support of phasing-out NPEs in industrial and household formulations.[6] As a result, candidates for NPE replacements are being sought. The nonionic surfactants described here based on the sulfoxide moiety were investigated as NPE replacements.

Surfactants containing sulfoxide functional groups have not been broadly studied. These surfactants were described in the mid-20th century in several patents.[7] Clint and Walker studied the behavior of sulfoxide surfactants in homologous and mixed micelles because of their “compact head groups”.[8] Iyota *et al.*’s work is a continuation to Clint and Walker, exploring non-ideal mixing of sulfoxide-containing surfactants and other nonionic surfactants.[9] Hennaux and Laschewsky reported a new group of polymerizable sulfoxide containing surfactants in 2001. The polymerization is not based on the hydrophilic groups, but rather the double bonds in the hydrophobe.[10] The current work marks the first time that esters or amides were used along with sulfoxide groups in a surfactant molecule.

In Chapter 4, nonionic surfactants derived from 2-hydroxy-4-(methylthio) butyric acid were studied. The structures of various molecules based on these synthetic steps were characterized with ^{1}H NMR. The properties of sulfoxide surfactants, such as CMC, γ_{CMC}, cloud temperature, Draves wetting kinetics, Ross-Miles foaming ability, foam collapse profile and laundry performance as nonionic surfactant in an enzyme and brightener containing liquid formulation were investigated and compared to other surfactants.

1.1.3 Nonionic surfactants with enhanced amphiphilicity

Nonionic surfactants containing ethylene oxide (EO) repeating units are widely formulated for their compatibility with other surfactants, low CMC and low γ_{CMC}. EOs are popular building blocks for the hydrophilic portion of nonionic surfactants because these groups are inexpensive, highly available, and compatible with other hydrophilic groups. In addition, adding such groups to alcohol moieties is chemically straightforward and the average number of ethylene oxide groups per molecule can be controlled. Alcohol ethoxylates (AEs) currently claim most of the nonionic market[4] and is replacing NPEs in many applications.[11] However, AEs sometimes form unwanted gels in water, which are problematic to formulation and applications. More AEs are often required for equivalent performance with NPEs as well.

As stated previously, Chapter 4 describes molecules containing sulfoxides as NPE replacements; however the molecules described in Chapter 4 had limited hydrophobic chain lengths because the molecule had only one sulfoxide unit. In Chapter 5, molecules containing more headgroup hydrophilicity were introduced via two routes. In one route, ethylene oxide units were added to the molecule. Instead of alcohols, alcohol ethoxylates were reacted with the 2-hydroxy-4-(methylthio) butyric acid. In another route, oligomeric sulfoxide headgroups can be produced through esterification, since 2-hydroxy-4-(methylthio) butyric acid contains both carboxyl and hydroxyl groups. The properties of these surfactants, such as CMC, γ_{CMC}, lower/upper critical solution temperatures, Draves wetting kinetics, Ross-Miles foaming ability, foam collapse profile and laundry performance as nonionic surfactant replacement in an enzyme-containing liquid formulation were investigated and compared to other surfactants.

1.2 Microemulsions

Microemulsions are thermodynamically stable emulsion of two phases, usually a water phase and an oil phase, homogenized with emulsifiers. The term “microemulsion” was first introduced by Schulman[12], but the sizes of the emulsion droplets in such mixtures were later found to be nanometer scales.

Nonionic surfactants are excellent for formulating microemulsions, because of their high hydrophobicity and insensitivity to electrolytes, especially multivalent ions. Other advantages of nonionic emulsifiers include higher adsorption capacity, low price and less foam.[13]

Nonionic surfactant microemulsions were first studied in the early 1970s,[14] in the light of early ionic surfactant microemulsion studies by Shulman and his co-workers[15]. Shinoda and Kunieda found that nonionic alcohol ethoxylates turn from water soluble to oil soluble in a microemulsion system upon raising temperature.[14b] Due to Bancroft’s rule[16], the microemulsion phases are switching correspondingly. Sottmann and Strey studied the ultralow interfacial tension (IFT) of ternary alcohol ethoxylated surfactants/n-alkane/water systems, and correlated the structures of surfactants and oils with the IFT and phase behaviors.[17] Salager et al. used octylphenol ethoxylates as the surfactant in microemulsion systems to correlate more physicochemical variables with microemulsion phase behaviors.[18] Based on the phase behavior studies above, a hydrophilic-lipophilic deviation (HLD) model of nonionic surfactant microemulsions was proposed, including the effect of temperature, oil content, aqueous salinity, surfactant structure and cosurfactants/linkers.[19]

1.2.1 Winsor's R ratio

A traditional model called Winsor R ratio model can help us understand microemulsion systems, which was proposed by Winsor[20] and later on improved by Bourrel and Schechter[21]:

$$R = \frac{A_{SO} - {}^{1}/_{2}\, A_{OO} - {}^{1}/_{2}\, A_{LL}}{A_{SW} - {}^{1}/_{2}\, A_{WW} - {}^{1}/_{2}\, A_{HH}} \qquad \text{Equation 1-1}$$

where the R is called the Winsor R ratio, A_{SO} (A_{SW}) is the interaction between the adsorbed surfactant at the interface and the oil (water) molecules, A_{OO} (A_{WW}) is the interaction between two oil (water) molecules, and A_{LL} (A_{HH}) is the interaction between two lipophiles (hydrophiles).

The criterion for optimum microemulsion is R=1, when the interaction of the surfactant to the oil and the water phases are balanced out by each other. R<1 and R>1 correspond with type I and II behaviors, respectively. The premise of Winsor's model is that the phase behavior at R=1 is determined by the magnitude of the numerator and the denominator in Equation 1-1. In other words, the stronger the interactions of the surfactant with both phases are, the lower minimum IFT will be reached, and hence the higher solubilization capacity.

1.2.2 Fish diagram

Figure 1-2 shows the “fish diagram” of nonionic surfactants including a pure $C_{12}EO_6$ and a technical grade $C_{12}EO_6$ which is made up of a mixture with different EO numbers and hydrophobe lengths.[22] The change of Types I-III-II microemulsions with temperature is only observed within a range of surfactant concentration. If the surfactant concentration is lower than the appropriate range of values, the middle phase microemulsion will not be observed even if PIT is reached. If the surfactant concentration is higher than the appropriate range of values, the bicontinuous microemulsion will become a single phase (type IV, thermodynamically stable single-phase water/oil mixture).

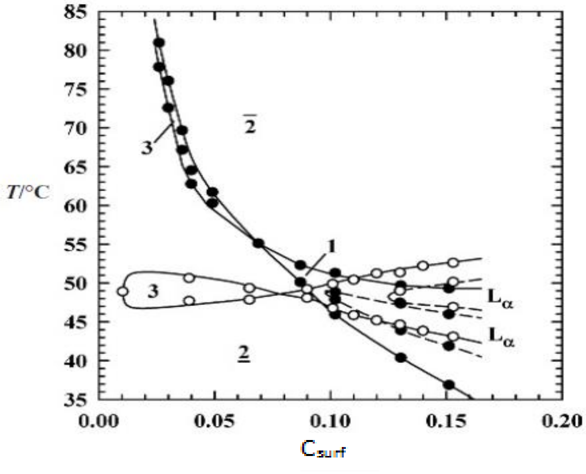


Figure 1-2 “Fish” diagram of nonionic surfactants vs. n-octane systems[22]; ○: $C_{12}EO_6$; ●: technical grade $C_{12}EO_6$ (mixture of different n_{EO} and n_{CH})

1.2.3 Hydrophilic-lipophilic difference (HLD) model

In order to describe the behavior of nonionic surfactant induced microemulsions, a model called the hydrophilic-lipophilic difference (HLD) model was proposed by Salager et al.:[18a, 19]

$$HLD = b * S - K(EACN) - f(A) + \sigma + c_T(\Delta T) \qquad \text{Equation 1-2}$$

where S is salinity, b is the salinity dependency, EACN is the equivalent alkyl carbon number, K is the coefficient of EACN, f(A) is a function of the consurfactant/linker type and concentration, σ is the characteristic curvature of the surfactant, ΔT is the temperature deviation from a reference (25°C) and c_T is temperature dependency. For primary alkanes, EACN is the number of hydrocarbon units. For oils other than primary alkanes, EACN is a characteristic number of the oil determined by microemulsion tests representing how hydrophobic the oil is. For EO-based nonionic surfactants, K is in the range of 0.1-0.2 for numerous surfactant-oil pairs, and c_T is typically around 0.06 T^{-1}. When HLD=0, the microemulsion is at its optimum state, when the IFT is the lowest and the SP is the highest. HLD can be translated to the chemical potential difference between the water and oil phase in the system. When HLD<0, the surfactant is more hydrophilic, and a type I microemulsion will be formed, and vice versa for HLD>0.

In Chapter 6, sulfoxide-based surfactants were used to formulate microemulsions. These surfactants are proposed to have excellent emulsifying ability, because the strong interaction between sulfoxide group and water suggests these surfactants may exhibit a high characteristic length, and hence high solubilization capacity.[23] The structural aspects of the sulfoxides indicating an enhanced emulsifying performance include a. the hydrocarbon-ester-sulfoxide structure of the ester sulfoxides resembles those of extended surfactants,[23a] and b. the high interaction of sulfoxide groups with water molecules due to its strong dipole point to high characteristic lengths, i.e., the interaction range on a length scale of surfactants at the oil/water interface. The HLD model parameters of the ester sulfoxide surfactants were studied by looking at the PIT of various oils, surfactant hydrophobe unit numbers and salt concentrations. The minimum IFTs of various surfactant/oil/water systems were measured.

Chapter 2 Experimental Procedures

2.1 Materials

2.1.1 2-hydroxy-4-(methylthio) butyric acid derived surfactants

The 2-hydroxy-4-(methylthio) butyric acid derived surfactants were synthesized by Novus International. Some surfactants were further purified with silica liquid chromatography columns. In the case for anionic surfactants, the samples were neutralized by ion-exchange columns.

Nomenclatures

The compounds that consist of a significant distribution of species, for example, ethoxylated ester sulfoxides (C_nEO_mESO), are italicized in the current dissertation to distinguish from the compounds that contain essentially one molecule. Schematic structures of 2-hydroxy-4-(methylthio) butyric acid, ester sulfide carboxylate sodium salt (C_nESCOONa), ester sulfoxide carboxylate sodium salt (C_nESOCOONa), monomer sulfoxide esters (C_nESO), oligomer sulfoxide esters (C_nESO_m), ethoxylated ester sulfides (C_nEO_mES) and ethoxylated ester sulfoxides (C_mEO_nESO) are shown in Figure 2-1. The samples are abbreviated so that the name represents all the functional groups in the surfactant structure. For example, $C_{12}EO_4ESO$ (3,6,9,12-tetraoxatetracosyl 2-hydroxy-4-(methylsulfinyl)butanoate) represents a mixture with the major content being the ester of 2-hydroxy-4-(methylthio) butyric acid reacted with a commercial AE surfactant, tetraoxyethylene lauryl ether, which contains a dodecyl chain (C_{12}), an oligomer with 4 repeating ethylene oxide units (EO$_4$) followed by partial oxidation of the sulfide moiety.

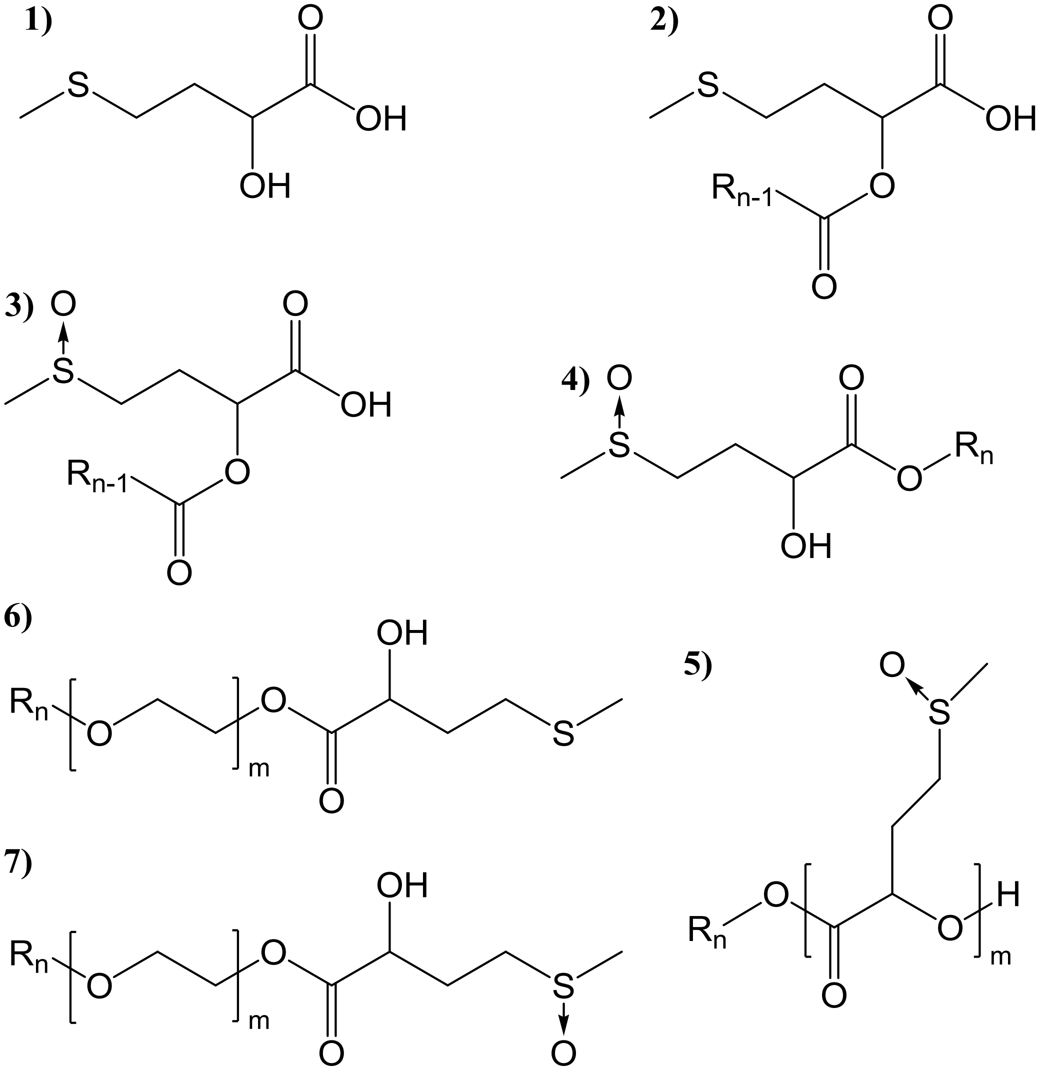


Figure 2-1 Structural schematics of various molecules used in this study. 1) 2-hydroxy-4-(methylthio) butyric acid, 2) ester sulfide acid (C_nESCOOH), 3) ester sulfoxide acid (C_nESOCOOH), 4) monomer ester sulfoxides (C_nESO), 5) oligomer ester sulfoxide (C_nESO$_m$), 6) ethoxylated ester sulfides (C_nEO$_m$ES), 7) ethoxylated ester sulfoxides (C_nEO$_m$ESO)

Ion-exchange neutralization

Ion exchange chromatography was used to neutralize the carboxylic acid (i.e., C_{12}ESCOOH, C_{12}ESOCOOH, etc.) instead of direct neutralization with alkali because of the susceptibility to hydrolysis of the ester group. A weakly acidic resin Dowex MAC-3 was used because of the weak acidity of the carboxylic group. In order to avoid precipitation during neutralization, a mixture of 70% ethanol and 30% water was used as a solvent. Dowex MAC-3 resin (proton form) was swollen and neutralized in excess NaOH/water solution, and then assembled into a column. After the resin was balanced with 2 column volumes of ethanol/water solvent, a 0.1g/ml acid solution was loaded then added and run through the resin 3-5 times for complete neutralization. Subsequently, the resin was rinsed with 2 column volumes (CV) of the ethanol/water solution, and the elution was collected. The solvent was then evaporated under vacuum at mild heat (40°C). Extra methanol was added 2-3 times to help remove water. The pH of the solution was raised from 4.1 to 7.5 after running through the column. The neutralized material was fully soluble in water (deionized with 18MΩ resistivity) while the unneutralized material was insoluble.

2.1.2 Other surfactants

Sodium dodecyl sulfate (>99%), sodium dodecylbenzenesulfonate (98%), hepta(oxyethylene) mono-*n*-dodecyl ether ($C_{12}EO_7$, >99%), hexa(oxyethylene) mono-*n*-dodecyl ether ($C_{12}EO_6$, >99%) and nona(oxyethylene) nonylphenyl ether (Igepal CO-630, NPE9 in average, Rhodia) were all purchased from Sigma-Aldrich. These surfactants were used without further purification.

2.1.3 Other materials

Sodium chloride (>99%), sodium bicarbonate (>99.7%), hydrogen peroxide (30%), sodium bisulfite (ACS reagent), ethanol (HPLC grade), methanol (HPLC grade), dodecyl chloride (>98%), hexadecyl chloride (98%), meta-chloroperoxybenzoic acid (mCPBA, 77%), 4-dimethylaminopyridine (DMAP, 99%), n-octanol (99%), n-decanol (>99%), n-dodecanol (>98%), n-tetradecanol (97%), n-hexadecanol (99%), n-octadecanol (99%) and dichloromethane (DCM, HPLC grade) were purchased from Sigma-Aldrich. Sodium hydroxide (>97%) was purchased from EMD. Toluene (99.5%) was purchased from VWR. Ethyl acetate (99.6%) was purchased from J.T.Baker. The low-foaming AE surfactant Plurafac SLF-180 (AE-LF) and the fluorescer Tinolux CBS-X were kindly provided by BASF. The protease, mannase and amylase were kindly provided by Novozymes. The PVP K30 and PVPNO Chromabond S403E were kindly provided by Ashland Inc. All the chemicals were used without further purification, except specified. Pre-soiled fabric swatches were purchased from Testfabrics Inc.. Silica gel liquid chromatography columns were purchased from Thomson Instrument Company.

2.2 Methods

2.2.1 Solid-liquid interface adsorption

Adsorption isotherms were performed on a hydrophilic surface (Aerosil 300, specific surface area=300m^2/g) and a hydrophobic surface (carbon nanotubes, SMW-100

[Southwest Nanotechnology], diameter=7.8 nm, length=735 nm, specific surface area=252 m^2/g). 5mL water solutions of surfactants at different concentrations were made and mixed with 75mg of adsorbent at room temperature. Mixtures were maintained at room temperature for 48h to reach equilibrium, and then the supernatant were characterized with HPLC (Aglient 1050; Phenomenex Kintex C18 column; methanol: water=80:20; flow rate 0.7mL/min; pressure: 220bar; UV detector at 210nm) to avoid any unwanted interference from contamination. The adsorption density was calculated with the equation:

$$\Gamma = Adsorption\ density = \frac{m_{sur,0} - m_{sur,super}}{A_{ads}} \qquad \text{Equation 2-1}$$

where $m_{sur,0}$ is the mass of surfactant in the solution before adsorption, $m_{sur,super}$ is the mass of surfactant in the supernatant after adsorption and A_{ads} is the surface area of adsorbent. Adsorption density was plotted against the equilibrium supernatant concentration. The supernatant concentration where the adsorptions density reaches maximum is the CMC. The adsorption isotherms were fitted with a two-step model described by the equations below considering both monomer adsorption and surface micellization:[24]

$$\Gamma = \frac{\Gamma_m k_1 C_e \left(\frac{1}{n} + k_2 C_e^{n-1}\right)}{1 + k_1 C_e (1 + k_2 C_e^{n-1})} \qquad \text{Equation 2-2}$$

where Γ_m is saturated adsorption density, k_1 is the equilibrium constant of monomer adsorption, k_2 is the equilibrium constant of surface micellization, C_e is the equilibrium surfactant constant and n is the average number of monomers in the surface micelles.

The standard free energy of monomer adsorption (ΔG_m^0) and surface micellization (ΔG_{sm}^0) was calculated from the equations below:

$$\Delta G_m^0 = -RTln(k_1) \qquad \text{Equation 2-3}$$

$$\Delta G_{sm}^0 = -\left({}^{1}/_{n}\right)RTln(k_2) \qquad \text{Equation 2-4}$$

2.2.2 Surface tension

Surface tension of the surfactant water solutions was determined with a Wilhelmy Plate tensiometer (Cahn DCA-322) at room temperature. Glass slides manufactured by Corning with a width of 22mm and thickness of 0.1mm were used as probes; the motor speed was set to be 100μm/s. The CMC was determined from the break point of γ vs. log C diagram. The C20 is the concentration at the intersection of γ vs. log C curve and the line of $\gamma = \gamma_{\text{pure water}}$ - 20mN/m.

2.2.3 Molecular interaction in micelles and surface monolayer

For binary surfactant mixtures, CMC at different mole fractions of the nonionic surfactant was analyzed according to Rubingh's one parameter model. In this model, the molecular interaction parameter (β) is used to describe the strength of the interactions. The constant β relates to the free energy change upon mixing[13]:

$$\Delta G_{mix} = \beta X(1 - X)RT \qquad \text{Equation 2-5}$$

where X is the mole fraction of surfactant 1 of the total surfactants in the mixture. The intermolecular interactions between two surfactants for mixed micelle or monolayer formation can be described by the following equations based on nonideal solution theory[25]:

$$\alpha C_{12} = \mathrm{X}\mathrm{C}_1 exp[\beta(1-\mathrm{X})^2] \qquad \text{Equation 2-6}$$

$$(1-\alpha)C_{12} = (1-\mathrm{X})\mathrm{C}_2 exp[\beta \mathrm{X}^2] \qquad \text{Equation 2-7}$$

where α is the mole fraction of surfactant 1 in total surfactants, X is the mole fraction of surfactant 1 in the mixed micelle or the air/liquid monolayer, C_1, C_2 are the CMC or the C20 of pure surfactants 1 and 2, and C_{12} is the CMC or the C20 of the mixture. When $\beta=0$ mixing in the micelle/monolayer is random, and when $\beta<0$ mixing is more alternating than random. When β is negative and $|\beta|>|\log(C_1/C_2)|$, there is synergism between the surfactants. The β parameter was calculated from mixed CMCs (β^M) and C20s (β^σ) with a custom-written Microsoft Visual Basic program.

2.2.4 Upper and lower critical solution temperatures

The cloud temperature (upper critical solution temperature, UCST) of the surfactant was determined according to ASTM D2024-09.[26] A 1.0 wt% surfactant solution was heated to 75°C, and then cooled at a 1°C/min rate to see if precipitation occurred. The solution was held at a temperature for at least 5 min, and then visually inspected. The temperature at which the precipitation disappeared was recorded as the UCST. For the Krafft temperature (lower critical solution temperature, LCST), the solutions were first cooled down to 4°C before it was heated.

2.2.5 Draves wetting

The Draves wetting test was run according to ASTM D2281-68.[27] 500 mL of surfactant solution was poured into a 500 mL graduated cylinder (38 cm in height), and 5.0 g of a standard skein hooked with a lead anchor was dropped in the solution. The skein floats in the solution because of the trapped air and sinks when wetted, and the time it took to sink after initially being added to the solution was recorded as the time of wetting.

2.2.6 Foaming

Ross-Miles

The Ross-Miles foam test was run according to the test protocol given by ASTM D1173-07.[28] 50mL of surfactant solution, also known as the receiver, was carefully poured into the 1 meter glass column, without creating any foam. A 200 mL pipette with the surfactant solution was placed 90cm above the receiver and the solution was allowed to drop into the foam receiver. The height of the foam produced was measured immediately and after 5 min.

Foam collapse profile

In order to study the foam collapse profile, an apparatus similar to that in Lunkenheimer et al.'s report was built.[29] A cylindrical glass funnel of 30mm inner diameter and 25cm length with a sintered glass G3 plate at the bottom was used. 50 mL of surfactant solution was slowly poured into the funnel without creating any foam. 50 mL of air was then injected with a syringe through the sintered glass plate at a 10 mL/min rate, to forcibly create 100 mL of foam. The volume of the entire air/liquid mixture (V_{total}) and that of the excess solution on the bottom (V_{excess}) was recorded. From V_{total} and V_{excess}, the volume of foam (V_f) and the volume of gas content in the foam (%gas) can be calculated.

$$V_f = V_{total} - V_{excess} \qquad \text{Equation 2-8}$$

$$\%gas = \left(1 - \frac{50mL - V_{excess}}{V_f}\right) \times 100\% \qquad \text{Equation 2-9}$$

A model of foam collapse profile considering gravitational draining and gas diffusion by Monslave and Schechter, and Lawrence et al.[30] was used to fit the foam profile data:

$$V_f = V_{f,initial} \cdot (C_A e^{-K_A t} + C_B e^{-K_B t}) \qquad \text{Equation 2-10}$$

$$C_A + C_B = 1 \qquad \text{Equation 2-11}$$

where 100mL is the total initial foam volume, C_A and K_A are the proportion and rate constant of foam collapse due to gas diffusion between bubbles and C_B and K_B are the proportion and rate constant of foam collapse due to gravitational draining.

2.2.7 Laundry performance

Laundry performance was evaluated with a terg-o-meter. The temperature was stabilized at 30°C with a water bath. The detergent according to the formulation given in Table 2-1 was dosed at 3g/L in 1L of tap water in the cylinder. The washing cycle was 20 min, followed by a 5 min rinsing cycle. The reflectance at 460 nm of the soiled fabrics was measured with a photoelectric colorimeter (HunterLab, UltraScan VIS) both before and after washing. The improvement in reflectance (ΔR) was used to characterize the laundry efficiency.

Table 2-1 Laundry formulation used to determine nonionic surfactant laundry performance

Ingredients	Content (wt%)
Fatty acid	0.2%
Sodium DETPMP	0.2%
Sodium citrate	5%
Sodium chloride	0.8%
Boric Acid	0.3%
Propylene glycol	3%
NaOH	2% (to pH=7-9)
Fluorescer	0.08%
Protease	0.4%
Mannase	0.15%
Amylase	0.4%
PVP	0.2%
PVPNO	0.2%
Nonionic surfactant	10%
Anionic surfactant	10%
Tap water	to 100%

The formulation was chosen to determine the performance of the nonionic surfactants as the nonionic component in a standard laundry formulation with enzymes and flourescers. Tests were done with fabrics pre-soiled with 7 different soils, including blood/ink/milk, tea, coffee, grass, wine, lipstick and chocolate drink. The soils were applied on two types of fabric substrates, cotton and a polyester/cotton=7/3 blend (PE/C).

2.2.8 Microemulsions

Phase inversion temperatures

In a ternary system with nonionic surfactant/water/oil, the surfactant and its concentration can be selected for the oil to form a microemulsion. When temperature is increased and the surfactant concentration is right, the microemulsion undergoes oil in water (O/W or type I), bicontinuous phase (type III/IV) and water in oil (W/O, or type II) emulsions. The reason for the change is that the surfactants become more hydrophobic with higher temperatures when hydrogen bonding becomes less important, and hence the interaction between surfactant and water (R denominator) is decreasing. Phase inversion temperature (PIT) is the temperature where R=1 in the ternary system, which is the middle point of the type III region and the minimum interfacial tension (IFT). In order to measure the PIT, an 1:1 (v:v) oil/water mixture with various surfactant concentrations ranging from 1 wt% to 5 wt% surfactant were made, and a water bath was used to control temperature. The temperature at which the emulsion changed from type I to type III or type III to type II was recorded as $T_{I/III}$ or $T_{III/II}$. The PIT is close to the middle point between $T_{I/III}$ and $T_{III/II}$.

Interfacial tension (IFT)

IFT is an important indicator of microemulsion quality, not only because it can be translated to the mechanical properties of microemulsion droplets, but also as it is related to the solubilization capability (SP=Mass of maximum solubilized oil or water/Mass of total surfactant), according to Chun Huh relationship[31]:

$$IFT = \frac{c}{SP^2} \qquad \text{Equation 2-12}$$

where c is called the Chun Huh constant, and is reported to be around 0.3mN/m for numerous systems.[32] Solubilization capacity, which is an important figure of microemulsion surfactants, indicates the surfactants' ability to homogenize incompatible phases. The lower the minimum IFT is, the higher SP can be, according to Equation 2-12. Usually, microemulsions are associated with ultralow IFTs below 10^{-2} mN/m.

Another reason to perform IFT measurements is the confirmation of PIT. PIT of a nonionic surfactant/water/oil system is the middle point of the $T_{I/III}$ and $T_{III/II}$, when the minimum IFT is reached. Due to the lack of accuracy in observing the microemulsions with human eyes, the PIT need to be confirmed with more quantitative ways. Therefore, the IFT between the oil and water phases at a given surfactant concentration can be measured at a series of temperatures to obtain the PIT. IFT measurements were performed with a spinning drop tensiometer. The principle of spinning drop measurements is illustrated in Figure 2-2.[33] The idea is to measure the radius of the spinning drop (R_m) at certain angular velocity (ω), and calculate the IFT with the following equation (Vonnegut Formula)[34]:

$$\gamma = \Delta\rho \cdot \omega^2 R_m^3 / 4 \qquad \text{Equation 2-13}$$

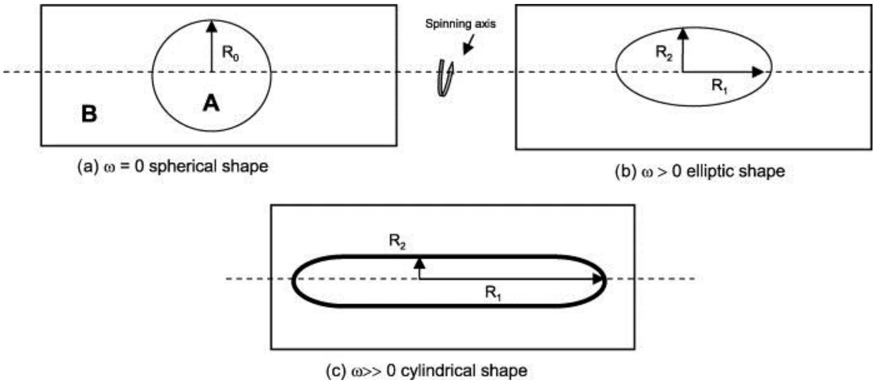


Figure 2-2 Illustration of relations between spinning and droplet shape in spinning drop tensiometry (from Viades-Trejo and Gracia-Fadrique, 2007)

Hydrophilic-lipophilic difference (HLD) model

In order to understand the characteristic behaviors of a surfactant in microemulsions, some of the parameters in the HLD model needs to be determined. Not all parameters need to be determined, for example, S can be zero if no salt is added to the water. If no cosurfactant is used, f(A) is 0 as well. Once the PITs of one surfactant vs. various oils are obtained, the parameters c_T/K and σ/K can be obtained from the re-written HLD equation when S=0 and f(A)=0:

$$EACN = {}^{c_T}/_{K} \cdot (PIT - 25) + {}^{\sigma}/_{K} \qquad \text{Equation 2-14}$$

σ/K is also known as the optimum EACN of an emulsifier; this ratio is equal to the EACN of the oil that forms an optimum microemulsion with the target surfactant at 25˚C with pure water. c_T/K is the PIT dependence of EACN for a target surfactant.

Individual parameters cannot be determined by just varying EACN; a second variable must be varied as well. Such second variable can be the surfactant structure, preferably the hydrophobe, because the interaction between the hydrophobe and the oil phase and their behaviors upon changing conditions should resemble other hydrocarbon based surfactants, such as AE surfactants. Surfactants with various hydrophobe sizes must be tested, in order to scale the HLD parameters to the change of hydrocarbon unit numbers. According to Acosta[35], the characteristic curvature of AE surfactants can be predicted by their structures:

$$\sigma = 0.28 \times N_{C,S} - N_{E,S} + 2.4 \qquad \text{Equation 2-15}$$

where $N_{E,S}$ is the number of EO units in the hydrophile and $N_{C,S}$ is the number of hydrocarbon units in the hydrophobe. Once a second set of σ/K is obtained, then Δσ/K (=σ_1/K-σ_2/K, assuming K is constant for the particular surfactant class) can be compared with Δσ (=$0.28 \times \Delta N_{C,S}$) to calculate K, and hence σ and c_T.

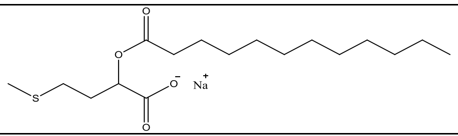
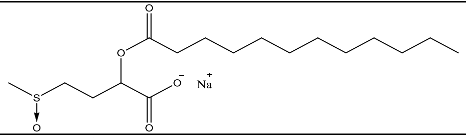
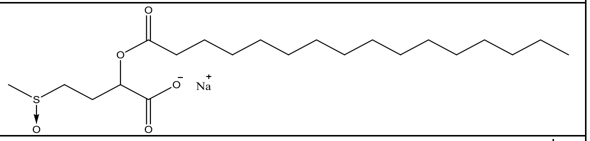
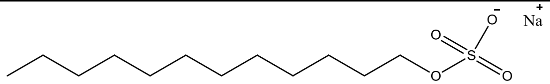
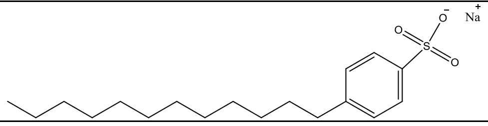
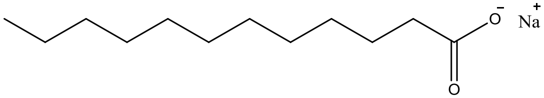
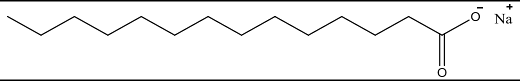
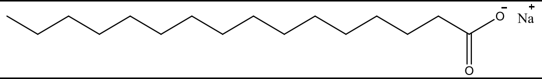
Chapter 3 Anionic Surfactants

3.1 Surfactants

3.1.1 Nomenclatures

The acronyms, chemical name and structures of the anionic surfactants discussed in this chapter are presented in Table 3-1.

Table 3-1 Anionic surfactants based on 2-hydroxy-4-(methylthio) butyric acid

Acronyms	Chemical Name	Structure
C_{12}ESCOONa	sodium 2-(dodecanoloxy)-4-(methylthio)butanoate	
C_{12}ESOCOONa	sodium 2-(dodecanoloxy)-4-(methylsulfinyl)butanoate	
C_{16}ESOCOONa	sodium 2-(hexadecanoloxy)-4-(methylsulfinyl)butanoate	
SDS	sodium dodecyl sulfate	
SDBS	sodium dedecylbenzene sulfonate	
NaL	sodium laurate	
NaMy	sodium myristate	
NaPa	sodium palmitate	

3.1.2 HPLC

The HPLC were performed in an Agilent 1260 system with acetonitrile / 2.5 mmol H_2SO_4 solvent and Dionex Acclaim® Organic Acid (OA 5µm, 120Å, 4 x 150mm) column. In order to confirm the integrity of the ester after the ion exchange chromatography, the salts were dissolved in water and analyzed by HPLC. The salts will be neutralized by the acid additive in the HPLC and the resulting chromatogram should look similar to the starting acid.

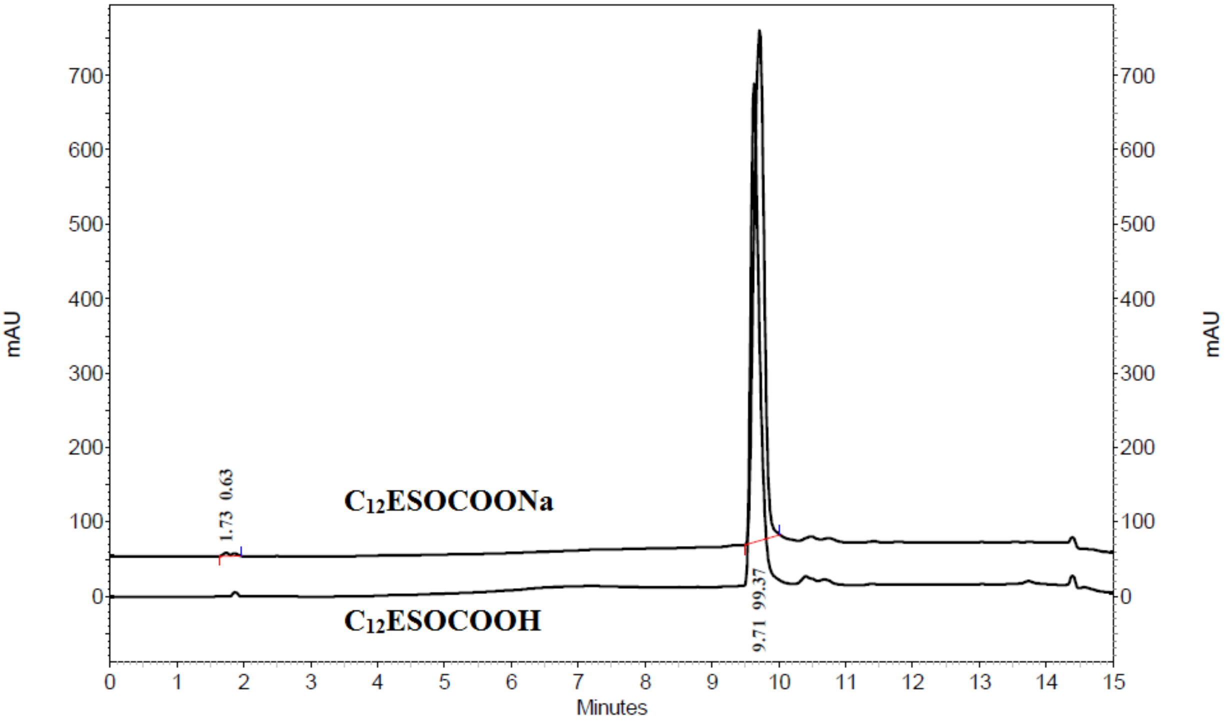


Figure 3-1 Overlay of HPLC traces of C_{12}ESOCOONa with C_{12}ESOCOOH

Figure 3-1 shows the HPLC of C_{12}ESOCOOH and C_{12}ESOCOONa with H_2SO_4 present in the solvent. Evidence of hydrolysis will be evident by the appearance of the sulfoxide of 2-hydroxy-4-(methylthio)butyric acid which has a retention time of 1.6

min. As can be seen from Figure 3-1, there is only a small amount of material present in the salt after ion exchange when compared to the starting acid. Therefore, the ion exchange chromatography had little effect on the integrity of the ester.

3.2 Surface chemical properties

Surface properties of C_{12}ESCOONa, sodium 2-dodecanoloxy-4-(methylsulfinyl)butanoate (C_{12}ESOCOONa) and 2-hexadecanoloxy-4-(methylsulfinyl)butanoate (C_{16}ESOCOONa) are presented in Table 3-2 in comparison to anionic surfactants with similar structures, including the linear carboxylates, sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS).

Table 3-2 Water solubility and surface chemical properties of various anionic surfactants

Surfactant	**Water Solubility (mM)**	**CMC (mM)**	**γ_{CMC} (mN/m)**	**pC20**	**CMC/C20**	**Γ_{max} (×10^{-10} mol/m^2)**	**a_{min}/ion (Å^2)**
C_{12}ESCOONa	282	1.0	35	3.84	5.55	2.10	40
C_{12}ESOCOONa	>1000	1.7	40	3.27	3.15	2.33	34
C_{16}ESOCOONa	117	0.54	42	4.07	4.56	1.26	65
SDS	350[36]	12.4[37] 8.0[38] 8.2[39]	40[37]	2.36[37]	2.6[37]	2.93[37]	57[37]
SDBS	575[40]	3.1	34	3.24	5.30	2.25	52[31]
NaL	90	19.1 28.1[41] 31.2[42] 27.2[43]	29[44] 30	3.32	38.5	1.06	78 47[31]
NaMy	6[45]	4.5(50°C)[38] 4.0[45] 6.9[46]	--	3.67	--	1.39	60
NaPa	--	2.1(30°C)[43] 1.8(62°C)[38]	--	--	--	--	--

Note: If not specified, all data are measured at room temperature, 1 atm; if not referenced, all data are measured in this study.

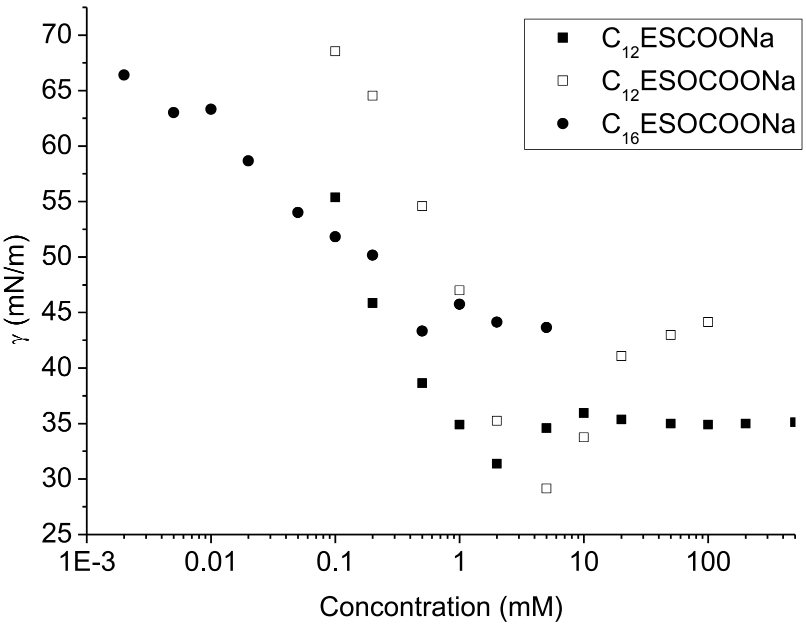


Figure 3-2 CMC determination of C_{12}ESCOONa, C_{12}ESOCOONa and C_{16}ESOCOONa via surface tension

Surface chemical properties of C_{12}ESCOONa, C_{12}ESOCOONa and C_{16}ESOCOONa were computed from the surface tension data in Figure 3-2. The slight undershoots near the CMCs are attributed to the presence of a small amount of impurity, possibly straight chain carboxylic acids and their sodium salts from the residue of the esterification reaction or hydrolysis during neutralization.

Relative to the solubility of sodium laurate (NaL) (0.02 g/ml) and sodium myristate (NaMy) (0.0015 g/ml), C_{12}ESCOONa's is much higher (0.1 g/ml). Comparing the molecular structure of C_{12}ESCOONa and NaMy in Figure 3-2, C_{12}ESCOONa has an additional ester group on the main chain and a methyl-sulfur-ethyl group as a branch. The combination increased the solubility by 2 orders of magnitude while lowering the

CMC by a factor of 4. The explanation is that the sulfur containing branch interferes with intermolecular arrangement and hence increases the solubility. At the same time, the additional three carbon atoms are able to overcome the hydrophilic effect of the ester group and the sulfur atom and increase the molecule's tendency to form micelles, i.e lower the CMC.

All CMCs of the sulfoxide/sulfide carboxylate surfactants based on 2-hydroxy-4-(methylthio) butyric acid are lower than that of SDS, SDBS, NaL, and NaMy measured at the same temperature, or sodium palmitate (NaPa) at higher temperatures. Sulfoxide/sulfide carboxylate surfactants also possess relatively high pC20, indicating high efficiency in lowering the surface tension. However, surface tensions at the CMC and surface excess concentrations are not superior to other anionic surfactants, suggesting comparable effectiveness of surface adsorption. The noticeable property is CMC/C20, which is an indicator of the tendency of liquid air adsorption versus micelle formation (the higher, the more inclined to surface adsorption). The reason that sulfoxide/sulfide carboxylate surfactants favor micelle formation more than its carboxylate counterpart might be a result of molecular geometry; sulfoxide/sulfide carboxylate surfactants have a bulkier head group and a straight chain hydrophobe which would favor spherical geometries. The anomaly is C_{16}ESOCOONa, which has a high surface area per molecule (i.e., low effectiveness), and a very high pC20 (i.e., high efficiency). The latter is to be expected since the carbon chain is longer, but the former is less likely since longer hydrophobe usually increases the adsorption effectiveness. Our suspicion is that the surface active impurities in this sample interfered with surface arrangement of C_{16}ESOCOONa.

The comparison between C_{12}ESCOONa and C_{12}ESOCOONa can be translated to the difference between sulfur and sulfoxide functional groups. Oxidation increased the water solubility and CMC, which was expected. The increase of surface tension at the CMC is usually the result of one of two reasons: a. high surface area per molecule (a_{min}) and b. low tendency of liquid/air interface participation versus micelle formation (CMC/C20). C_{12}ESOCOONa has both a lower a_{min} and a lower CMC/C20, suggesting that the latter is true. The reason sulfoxide surfactant favors micelle formation relative to air-liquid adsorption is unknown.

3.3 Surfactant phase behavior

The precipitation tendencies of sulfoxide/sulfide carboxylate surfactants are presented in Table 3-3 in comparison with common anionic surfactants.

Table 3-3 Krafft point and calcium tolerance of sulfoxide/sulfide carboxylate surfactants with comparisons

Sample Name	Krafft Point (°C)	$CaCl_2$ Tolerance (µM)	Hardness Tolerance (ppm as $CaCO_3$)
C_{12}ESCOONa	<4	100	10
C_{12}ESOCOONa	<4	5000	500
C_{16}ESOCOONa	<4	100	10
NaL	13[47]	0.5	0.05
SDS	15[38], 16[42]	40[44]	4[44]

Note: if not referenced, all data are measured in this study.

3.3.1 Krafft point

Within 48 hours, 1 wt.% solutions of C_{12}ESCOONa, C_{12}ESOCOONa nor C_{16}ESOCOONa did not show precipitation in the 4°C water bath, and hence the Krafft points of all three sulfoxide/sulfide carboxylate surfactants are lower than 4°C. Based on the reported data, the sulfoxide/sulfide carboxylate salts have better low temperature operability than SDS (Krafft point at 15°C).

3.3.2 Calcium tolerance

In terms of hardness tolerance, the C_{12}ESCOONa solution showed precipitate with $CaCl_2$ only above 100µM. NaL and SDS were also tested; the results show that the C_{12}ESCOONa has approximately 2.5 orders of magnitude better calcium tolerance than the linear carboxylate (which agrees with the water solubility data) and about half an order of magnitude better than the linear sulfate, SDS. The improved hardness tolerance is a combined effect of the increased hydrogen bonding due to the ester group and the sulfur atom, and the branching in the head group. Oxidation of the sulfur atom further improved its hardness tolerance. C_{12}ESOCOONa has a hardness tolerance of 5000 mM of $CaCl_2$, which is a factor of 50 better than the unoxidized form. In fact, the increased hardness tolerance from sulfur oxidation is exactly offset by 4 additional hydrocarbon units, by comparing the data of C_{12}ESCOONa and C_{16}ESOCOONa. Due to its good water solubility, low CMC and high hardness tolerance, C_{12}ESOCOONa is a potential calcium tolerant anionic surfactant and a candidate to be a builder in hard water formulations.

3.4 Draves wetting test

For the Draves wetting test, 0.1 wt.% surfactant solutions were used for all the surfactants. As presented in Table 3-4, C_{12}ESCOONa outperforms NaL in the wetting time with a comparable performance to SDS. Since C_{12}ESCOONa is a larger molecule than NaL and SDS, it should have a smaller diffusion coefficient and hence a higher wetting time. One explanation is that C_{12}ESCOONa adsorbs more strongly to the interface so that a higher fraction of each collision of the molecule with the interface results in adsorption.

Table 3-4 Draves wetting test results of sulfoxide/sulfide carboxylate surfactants with comparisons

Sample Name	Draves wetting time (s) of 0.1 wt% solution
C_{12}ESCOONa	11
NaL	52
SDS	11

3.5 Ross-Miles foaming test

For the Ross-Miles foam test, all surfactants were used at 1 wt.% concentration, which is above all CMCs. The results in Figure 3-3 show that the C_{12}ESCOONa generates foam comparable to the reference anionic surfactants (measured in our laboratory using the identical equipment and procedure), but dissipates much faster. Fast dissipation indicates lack of surface cohesiveness. Judging from its structure, the branch could have disturbed the surface arrangement of surfactant molecules. Quick dissipation of foams is a desirable property in automatic dishwashing and laundry, which is another possible application suggested by sulfoxide/sulfide carboxylate surfactants.

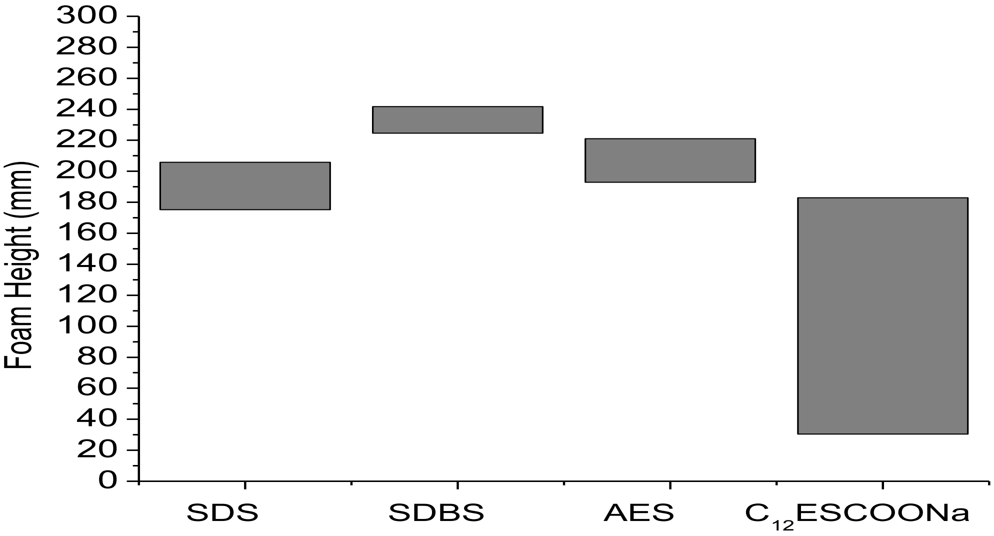


Figure 3-3 Ross-Miles foam test results of C_{12}ESCOONa comparing with SDS, SDBS, AES (alkyl ether sulfate, a commercial sample Steol CS-460). Top of the bars correspond to the initial height of foam; the bottom of the bars correspond to the foam height after 5 mins.

3.6 Summary

A family of anionic surfactants, sodium 2-alkanoloxy-4-(methylthio)butanoate or sodium 2-alkanoloxy-4-(methylsulfinyl)butanoate, were successfully synthesized. This family have good water solubility, low Krafft point, high surface tension reduction efficiency, low critical micelle concentrations and improved calcium tolerance compared to sodium laurate and sodium dodecyl sulfate. The solutions of the surfactants have comparable wetting performance as sodium dodecyl sulfate, which exceeds that of sodium laurate. The surfactant generates foam roughly equivalent with similar anionic surfactants, which dissipates much more quickly. The combination of the improved critical micelle concentration, Krafft point, calcium tolerance, wetting time and foam dissipation shows the new surfactant has some promise in detergency formulations.

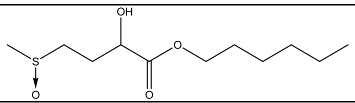
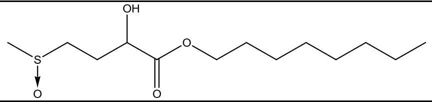
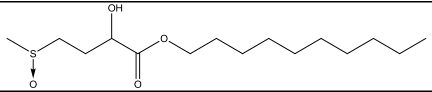
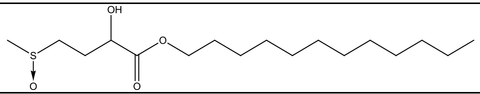
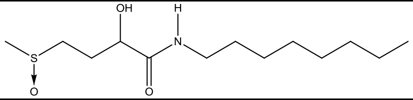
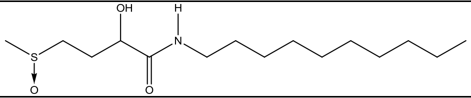
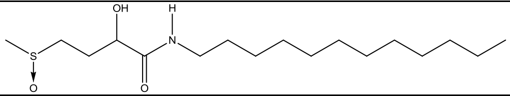
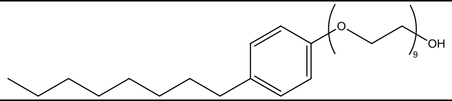
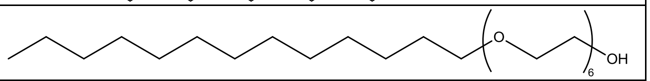
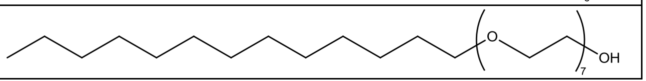
Chapter 4 Nonionic Surfactants

4.1 Surfactants

4.1.1 Nomenclatures

The acronyms, chemical names and schematic structures of the sulfoxide esters/amides derived from 2-hydroxy-4-(methylthio) butyric acid are shown in Table 4-1.

Table 4-1 Nonionic surfactants based on 2-hydroxy-4-(methylthio) butyric acid

Sample Acronym	Chemical Name	Structure
C_6ESO	hexyl 2-hydroxy-4-(methylsulfinyl)butanoate	
C_8ESO	octyl 2-hydroxy-4-(methylsulfinyl)butanoate	
$C_{10}ESO$	decyl 2-hydroxy-4-(methylsulfinyl)butanoate	
$C_{12}ESO$	dodecyl 2-hydroxy-4-(methylsulfinyl)butanoate	
C_8ASO	octyl 2-hydroxy-4-(methylsulfinyl)butanamide	
$C_{10}ASO$	decyl 2-hydroxy-4-(methylsulfinyl)butanamide	
$C_{12}ASO$	dodecyl 2-hydroxy-4-(methylsulfinyl)butanamide	
NPE9	nona(oxyethylene) nonylphenylether	
$C_{12}EO_6$	hexa(oxyethylene) mono-n-dodecyl ether	
$C_{12}EO_7$	hepta(oxyethylene) mono-n-dodecyl ether	

Schematic structures of 2-hydroxy-4-(methylthio) butyric acid, the sulfoxide esters and the sulfoxide amides are shown in Table 4-1. As presented in Table 4-2, octyl 2-

hydroxyl-4-(methylsulfinyl)butanoate (C_8ESO) or 2-hydroxyl-4-(methylsulfinyl)-*n*-octylbutanoamide (C_8ASO) and their analogues with longer hydrocarbon chains, namely decyl 2-hydroxyl-4-(methylsulfinyl)butanoate (C_{10}ESO), 2-hydroxyl-4-(methylsulfinyl)-*n*-decylbutanoamide (C_{10}ASO), dodecyl 2-hydroxyl-4-(methylsulfinyl)butanoate (C_{12}ESO) or 2-hydroxyl-4-(methylsulfinyl)-*n*-dodecylbutanoamide (C_{12}ASO) were mixed, because the dodecyl-/decyl-ester/amide sulfoxides are not water soluble alone at room temperature. The mixtures were named to indicate the type and fraction of the contents, as summarized in Table 4-2. For example, *C_8/C_{10}ESO-mix* represents a mixture of 70 wt% of C_8ESO and 30 wt% of C_{10}ESO.

Table 4-2 Contents and fraction of mixtures of sulfoxide ester/amide nonionic surfactants

Mixtures	Contents (wt%)	Average Carbon Number Post Ester/Amide Groups
C_8/C_{10}ESO-mix	C_8ESO (70%) and C_{10}ESO (30%)	8.6
C_8/C_{12}ESO-mix	C_8ESO (70%) and C_{12}ESO (30%)	9.1
C_8/C_{10}ASO-mix	C_8ASO (60%) and C_{10}ASO (40%)	8.8
C_8/C_{12}ASO-mix	C_8ASO (75%) and C_{12}ASO (25%)	8.9

4.1.2 HPLC

The HPLC were performed in an Agilent 1260 system with acetonitrile as solvent and Dionex Acclaim® Organic Acid (OA 5μm, 120Å, 4 x 150mm) column. In order to confirm the purity of the surfactants after the ion exchange chromatography, the salts were dissolved in water and analyzed by HPLC. The purity of the main components were characterized by the peak area.

Table 4-3 Purity of the nonionic surfactants determined by HPLC

Compound	HPLC purity by area %
C_6ESO	98.2
C_8ESO	98.9
$C_{10}ESO$	98.5
$C_{12}ESO$	94.1
$C_{12}ESO_2$	94.9
$C_{14}ESO_2$	98.3
$C_{16}ESO_2$	99.3
$C_{18}ESO_2$	99.5

Table 4-3 shows the HPLC determined purity of C_6ESO, C_8ESO, $C_{10}ESO$ and $C_{12}ESO$. All the surfactants presented purity level above 98%, except for $C_{12}ESO$ with a 94.1% purity.

4.2 Surface chemical properties

Results of the surface tension vs. concentration measurements are presented in Figure 4-1 and Figure 4-2.

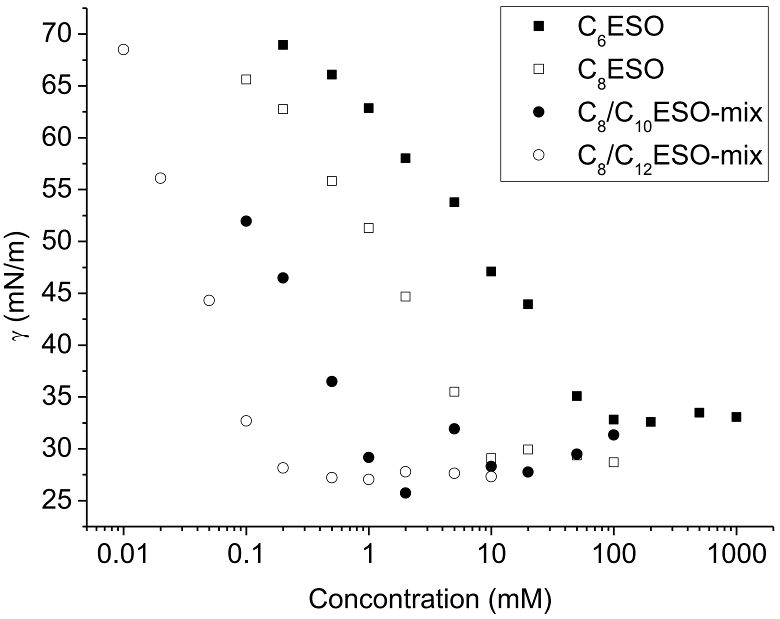


Figure 4-1 CMC determination of C_6ESO, C_8ESO, *C_8/C_{10}E-mix* and *C_8/C_{12}ESO-mix* via surface tension

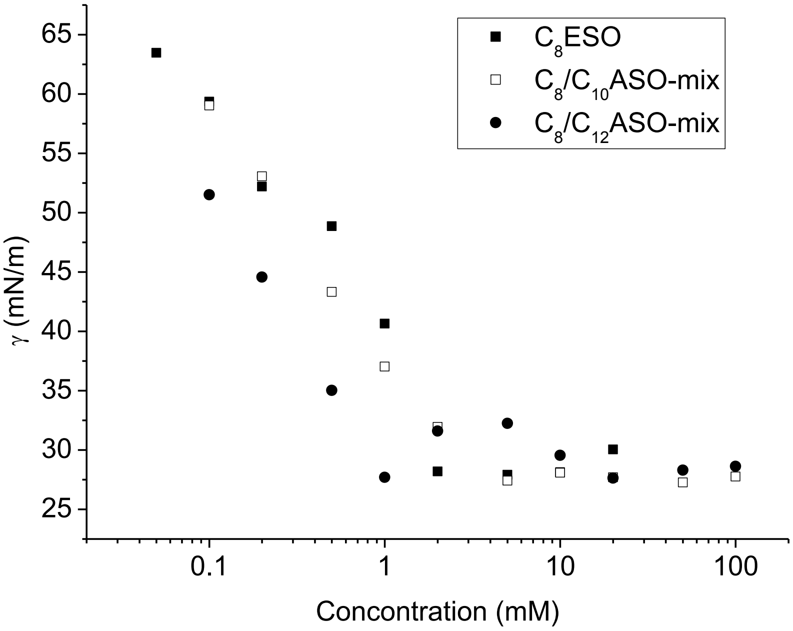


Figure 4-2 CMC determination of C_8ASO, *C_8/C_{10}ASO-mix* and *C_8/C_{12}ASO-mix* via surface tension

Surface chemical properties, including CMC, surface tension at CMC (γ_{CMC}), pC20, CMC/C20, surface excess concentration (Γ_{max}) and minimum area per molecule at the interface (a_{min}),[13] were calculated from the γ vs. log C diagrams and are presented in Table 4-4.

Table 4-4 Surface chemical properties of sulfoxide surfactants and their mixtures comparing with NPE9 and $C_{12}EO_7$

Surfactants	**CMC (mM)**	**CMC (wt%)**	**γ_{CMC} (mN/m)**	**pC20**	**CMC/C20**	**Γ_m (μmol/m^2)**	**a_{min} (Å^2)**
C_6ESO	104	2.6	33	2.4	23.9	2.5	66.9
C_8ESO	11.7 9.4^{AD}	0.33	29	3.2	17.5	3.3	50.8 34.5^{AD}
C_8/C_{10}ESO-mix	1.1	0.037	28	4.0	12.5	4.1	41.0
C_{10}ESO	0.59*	0.018*	--	--	--	--	--
C_8/C_{12}ESO-mix	0.11	0.0032	27	4.5	9.9	4.8	34.5
C_{12}ESO	0.060*	0.0020*	--	--	--	--	--
C_8ASO	6.9	0.29	29	3.3	15.4	3.5	47.3
C_8/C_{10}ASO-mix	2.9	0.084	28	3.7	14.6	3.7	44.4
C_{10}ASO	1.8*	0.055*	--	--	--	--	--
C_8/C_{12}ASO-mix	0.39	0.011	30	4.4	10.4	3.9	42.4
C_{12}ASO	0.16*	0.0053*	--	--	--	--	--
NPE9	0.038 0.078^{AD}	0.0038	33	5.8	26.5	2.1	79.4 61.1^{AD}
$C_{12}EO_7$[48]	0.082	0.0041	34	5.3	14.9	2.9	57

Note: all data, if not referenced, were measured in our labs by surface tension measurement

AD: measured by adsorption at the solid/liquid interface. CMC is the bulk concentration when adsorption reaches maximum

*: extrapolated from the CMCs of C8ESO and the mixtures, assuming that β in the mixtures are all 0

For calculation of Γ_m and a_{min} of the mixtures, the surfactant mixtures were treated as single component compounds. CMCs of C_{10}ESO and C_{12}ESO were extrapolated from the CMCs of C_8ESO, *C_8/C_{10}ESO-mix* and *C_8/C_{12}ESO-mix* using regular solution theory, assuming that mixing was ideal in the micelle phase (β^M=0). Both C_nESO and C_nASO followed Traube's rule[49] in that every two additional hydrocarbon unit in the main hydrophobic chain decreases the CMC by roughly an order of magnitude. With increasing hydrocarbon content, the surface tension reduction efficiency (pC20) and effectiveness ($-\gamma_{CMC}$) increased as expected while the surface area per molecule (a_{min}) decreased. The tendency to form micelles versus surface adsorption (-CMC/C20) also increased with increasing hydrophobic chain length. Comparison of esters and amides indicate that the identity of these two functional groups did not affect surface chemical properties. *C_8/C_{12}ESO-mix* and *C_8/C_{12}ASO-mix* showed CMCs comparable to or lower than hepta(oxyethylene) mono-*n*-dodecyl ether ($C_{12}EO_7$, AEs) and a commercial NPE surfactant (Igepal CO-630) with main component nona(oxyethylene) nonylphenyl ether (NPE9). Besides their smaller molecular weight, the sulfoxide esters/amides showed lower a_{min} at the liquid-air interface than the ethoxylates, in compliance with Clint and Walker's statement that sulfoxide headgroups are compact.[8b] *C_8/C_{12}ESO-mix* and *C_8/C_{12}ASO-mix* also presented higher micelle formation tendencies (-CMC/C20) than *NPE9* and $C_{12}EO_7$, which is also indicative of lower CMCs.

4.3 Adsorption at the Solid-Liquid Interface

Figure 4-3 presents adsorption isotherms of C_8ESO, *NPE9* and hexa(oxyethylene) mono-*n*-dodecyl ether ($C_{12}EO_6$, AEs) at solid/liquid interfaces. The CMC and a_{min} of C_8ESO and *NPE9* were obtained from the curve with the latter assuming monolayer adsorption, and compared to those at the air-water interface in Table 4-4. CMCs measured on the two interfaces were comparable, but the a_{min} were lower at the solid-liquid interface, which was to be expected if surface micellization or double layer adsorption occurred at the solid-liquid interface.

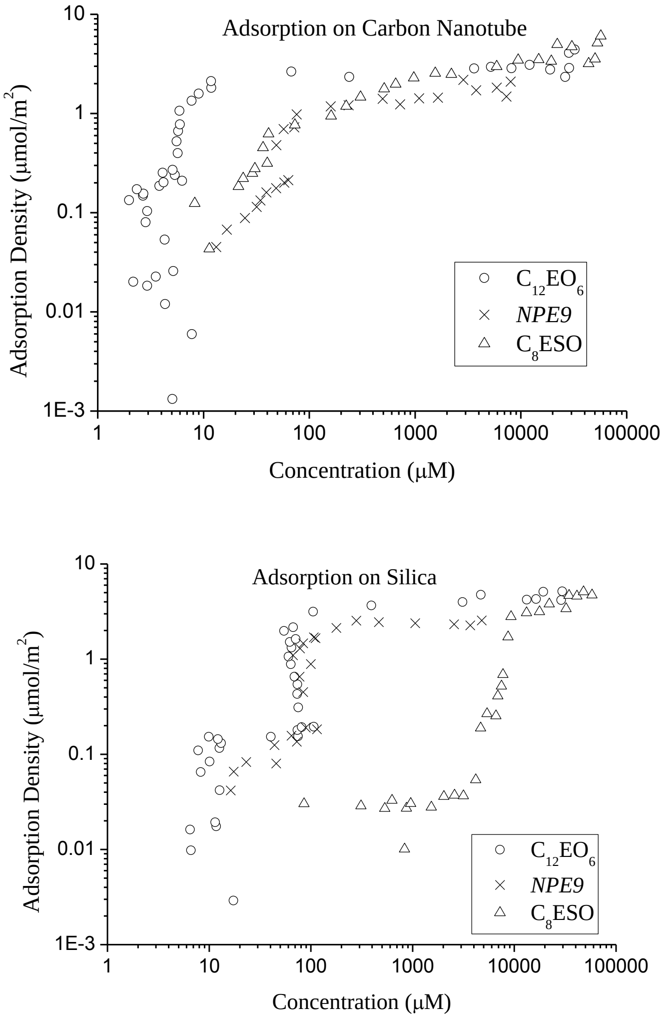


Figure 4-3 Adsorption density of C_8ESO, *NPE9* and $C_{12}EO_6$ on carbon nanotube (top) and silica (bottom)

These adsorption isotherms were further studied by applying a two-step model[24], which takes both monomer adsorption and surface micellization into account. The model parameters of the isotherms are presented in Table 4-5.

Table 4-5 Parameters in two-step adsorption model of C8ESO and other nonionic surfactants on two solid surfaces

Substrates	**Surfactants**	**Γ_m (μmol/m^2)**	**k_1**	**k_2**	**n**	**$\Delta G_m^0/RT$**	**$\Delta G_{sm}^0/RT$**
SMW-100	*NPE9*	1.71	1.76×10^4	4.02×10^{23}	6.7	-9.8	-8.1
SMW-100	$C_{12}EO_6$	2.96	1.89×10^5	2.06×10^{41}	9.2	-12.1	-10.3
SMW-100	C_8ESO	4.10	1.07×10^4	6.68×10^3	2.5	-9.3	-3.5
Aerosil-300	*NPE9*	2.34	1.53×10^4	1.38×10^{32}	9.5	-9.6	-7.8
Aerosil-300	$C_{12}EO_6$	4.15	4.95×10^4	1.00×10^{65}	17.4	-10.8	-8.6
Aerosil-300	C_8ESO	4.20	1.38×10^2	1.24×10^{26}	13.6	-4.4	-4.9

The saturated adsorption density (Γ_m) on both surfaces followed the relationship $C_8ESO>C_{12}EO_6>$*NPE9*, which is the reverse trend of a_{min} at the air/water interface. The ethoxylated surfactants have higher adsorption density on silica than carbon nanotubes. Both the standard free energy of monomer adsorption ($-\Delta G_m^0$) and surface micellization ($-\Delta G_{sm}^0$) followed the sequence $C_{12}EO_6>$*NPE9*$>C_8ESO$ on the surfaces. Based on the curves, the slope of the isotherms at both the monomer adsorption and surface micellization regions followed the same trend. $-\Delta G_m^0$ positively correlates with the length of the hydrophobes of the surfactants, and is lower on the hydrophilic surface than the hydrophobic surface for the same surfactant. C_8ESO has the shortest hydrophobe, and $C_{12}EO_6$ is a more pure compound than *NPE9* used in the current study, which explains why $-\Delta G_{sm}^0$, or the slope of isotherm was ranked as $C_{12}EO_6>$*NPE9*$>C_8ESO$.

4.4 Mixtures with anionic surfactants

Table 4-6 presents the molecular interaction parameters between C8ESO and two anionic surfactants, sodium dodecyl sulfate (SDS) and 4-(methylsulfinyl)-2-(dodecyl)butyric acid, sodium salt (C_{12}ESOCOONa). C_{12}ESOCOONa is a sulfoxide-based anionic surfactant reported by Grady *et al.* in an earlier manuscript.[50] β^M is the interaction parameter in the micelle phase and β^σ is the interaction parameter in the liquid-air monolayer. The extended application of the Rubingh's molecular interaction model[25a] to the surface monolayer was proposed and done by Rosen and Hua[25b]. The more negative the β is, the more attractive the surfactants are in this phase. Mixing of both the surfactant pairs favored micelle formation and surface tension reduction based on negative βs. Synergies were stronger, i.e. β was more negative, for micelles vs. the surface monolayer, which is the opposite of most ethylene oxide based surfactants.[13] This result suggests that loose micelles were formed by C8ESO, where additional hydrophobes can be easily inserted, and in a planar formation there might be less steric effect between the tail groups. The synergy of C_8ESO with C_{12}ESOCOONa was higher than with SDS.

Table 4-6 Molecular interaction parameters between C_8ESO and two anionic surfactants

Surfactants	**β^M**	**β^σ**
C_8ESO/SDS	-1.2	-0.4
C_8ESO/C_{12}ESOCOONa	-1.9	-0.1

4.5 Cloud Temperature

As shown in Table 4-7, sulfoxide surfactants have no observable cloud temperatures below 75°C, except those of *C_8/C_{10}ESO-mix* and *C_8/C_{12}ESO-mix*, which are still higher than *NPE9* and comparable to $C_{12}EO_7$.

Table 4-7 Cloud temperature of sulfoxide surfactants and their mixtures

Sample	**Cloud Temperature (°C)**
C_6ESO	>75
C_8ESO	>75
C_8/C_{10}ESO-mix	60
C_8/C_{12}ESO-mix	57
C8ASO	>75
C_8/C_{10}ASO-mix	>75
C_8/C_{12}ASO-mix	>75
NPE9	53
$C_{12}EO_7$[51]	58.5

Phase separation at the cloud temperature is explained as a sharp increase in aggregation number,[52] which happens when the surfactant critical packing parameter[53] (V_H/l_ca_0, where V_H is the volume in the micelle core taken by the hydrophobe, l_c is the length of the hydrophobe and a_0 is the area occupied by the hydrophilic group at the interface) approaches 1.[53c] A high cloud point of a nonionic surfactant is attributed to a small critical packing parameter and low aggregation number at room temperature.[13] The high cloud temperatures of these sulfoxide surfactants were a combination of three factors: straight chain hydrophobic groups, which lead to lower packing parameter; multiple hydrophilic groups in the hydrophilic groups favoring lower aggregation number and the sulfoxide's high tendency to form hydrogen bonds with water.[54] Higher cloud temperatures of the sulfoxide based surfactants mean wider operable temperature windows and easier formulation.

4.6 Draves wetting test

Table 4-8 presents the Draves wetting performance of the surfactant solutions. C_8ESO and *C_8/C_{10}ESO-mix* have comparable wetting performance at or above their CMCs as compared to NPE9.

Table 4-8 Draves wetting performance of sulfoxide ester surfactants comparing with SDS and *NPE9*

Wetting agent	**t_{sink} (s) @ 0.50%**	**t_{sink} (s) @ 0.25%**	**t_{sink} (s) @ 0.10%**	**t_{sink} (s) @ 0.05%**	**CMC (wt%)**
C_6ESO	>300	>300	>300	>300	2.6
C_8ESO	instant	5	>300	>300	0.33
C_8/C_{10}ESO-mix	instant	6	8	>300	0.037
C_8/C_{12}ESO-mix	12	21	55	>300	0.0032
SDS	instant	7	11	68	0.23
NPE9	instant	7	12	30	0.0092

C_8/C_{12}ESO-mix wetting kinetics were slower than *NPE9*, and surprisingly even slower than C_8ESO. The observed wetting kinetics are influenced by two factors: a thermodynamic component which is represented by the contact angle (surface tension) of the solution on the substrate and a kinetic component which is represented by the diffusion of the molecules at the wetting front when the surfactants are being depleted.[13] Since the diffusional kinetics should be determined by smaller molecules in the mixtures, the *C_8/C_{12}ESO-mix* should have had a similar diffusion constant as C_8ESO alone. The anomaly requires more study. All the sulfoxide surfactants had dramatically

slower wetting times when the concentration was lowered from 0.10 wt% to 0.05 wt%. Since the adsorption density was very high due to the low a_{min} of sulfoxide ester surfactants, perhaps a larger number of moles of surfactant vs. the NPE was required to wet the fabric sufficiently to cause it to sink, and hence mass transfer limitations were the fundamental cause of the slower wetting time.

4.7 Foaming ability and stability profile

4.7.1 Ross-Miles foaming test

Table 4-9 presents Ross-Miles foaming ability and foam stability of 1.0 wt% aqueous surfactant solutions. C_6ESO presented very low foam, possibly because of its high CMC. C_8ESO created significant foam that dissipated rapidly after 5 min, while all mixtures created and maintained foam well. C_8ESO may have too short a hydrophobe to form a cohesive surface monolayer for foam stabilization.

Table 4-9 Ross-Miles foaming property of sulfoxide surfactants and their mixtures comparing to SDS and *NPE9*

Sample	**Foam Height (mm)**	
	t=0min	**t=5min**
C_6ESO	23	2
C_8ESO	213	49
C_8/C_{10}ESO-mix	206	152
C_8/C_{12}ESO-mix	236	198
C_8ASO	194	99
C_8/C_{10}ASO-mix	219	196
C_8/C_{12}ASO-mix	213	158
SDS	206	175
NPE9	191	162

4.7.2 Foam collapse profile

Figure 4-4 shows the foam collapse profile of 1.0 wt% surfactant water solutions. Foam collapse profiles were fitted with the model described in the experimental section, and the parameters are presented in Table 4-10.

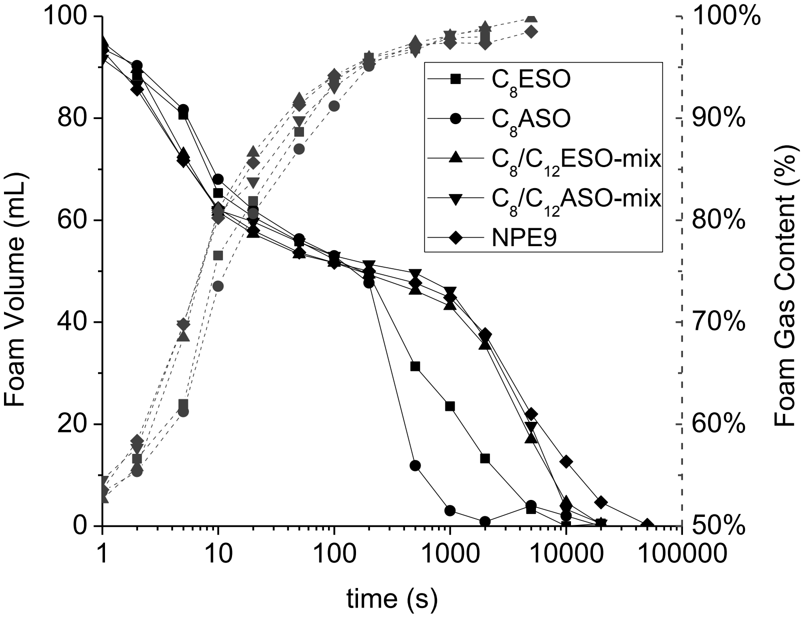


Figure 4-4 Foam collapsing profile: foam volume (solid) and gas content (dashed) in the foam of 1.0 wt% water solutions of C_8ESO, C_8ASO, *C_8/C_{12}ESO-mix*, *C_8/C_{12}ASO-mix* and *NPE9*

The foams decreased in height rapidly in the first 10s due to liquid drainage, and then the decrease slowed. Beyond 10s, the foams dissipated slowly because of gas diffusion through lamellae. The start of diffusion coincided with liquid draining in lamellae effectively ceasing and %gas (see Equation 2-9) stopping increasing. In the initial 100s, the foams of C_8ESO and C_8ASO was higher than those of *C_8/C_{12}ESO-mix*, *C_8/C_{12}ASO-mix* and *NPE9*, and the %gas of the former two foams are smaller than the latter two. The observation that draining of C_8ESO and C_8ASO are slower coincides with Dreger et al.'s work that the surfactants with faster diffusion rates creates higher initial foams in Ross-Miles foaming tests.[55] Rosen argued that quick diffusion of surfactants to the surface helps to lower the surface tension, and hence maintain the large air-water surface area in the initial foam.[13]

Table 4-10 Parameters of the foam collapse profile of C_8ESO, C_8ASO, *C_8/C_{12}ESO-mix*, *C_8/C_{12}ASO-mix* and *NPE9*

Surfactants	C_A (Diffusion)	K_A ($\times 10^{-3}$ s^{-1}) (Diffusion)	C_B (Draining)	K_B (s^{-1}) (Draining)
C_8ASO	0.55	4.5	0.45	0.11
C_8ESO	0.56	0.90	0.44	0.13
C_8/C_{12}ASO-mix	0.56	0.22	0.44	0.20
C_8/C_{12}ESO-mix	0.52	0.22	0.48	0.15
NPE9	0.53	0.18	0.47	0.18

Gas diffusion occurred much faster in C_8ESO and C_8ASO foams than in *C_8/C_{12}ESO-mix* and *NPE9*, and both the former two foams have higher C_A as well. In total, the collapsing rate of the five foams goes in the order: C_8ASO > C_8ESO > *C_8/C_{12}ESO-mix* ≈ *C_8/C_{12}ASO-mix* > *NPE9*, which agrees with the order of K_A, or the air diffusion rate. The permeability to air of the lamellae can be related to the arrangement of the surface monolayer and the thickness of the lamellae. C_8ASO and C_8ESO have larger a_{min} and shorter hydrophobic chains, and hence faster gas diffusion in their foams. *NPE9* has a large a_{min}, but also larger and more flexible head groups and longer (C_{12}) hydrophobes, which can lead to a tighter and more elastic monolayer. Therefore, the NPE9 foam was the most stable to diffusion. C_8ASO foam presented a much higher diffusion rate than the other surfactants. The difference between amide and ester groups should not be the reason since *C_8/C_{12}ESO-mix* and *C_8/C_{12}ASO-mix* presented essentially the same foam collapsing profiles. The outlying behavior of C_8ASO might be due to some trace amount of foam-destabilizing impurities.

4.8 Laundry performance

Laundry performance tests were done to evaluate the performance of *C_8/C_{12}ESO-mix* replacing *NPE9* in a liquid laundry formulation. The enzyme containing liquid laundry formulation used in the current study is presented in Table 2-1. The reflectance improvement (ΔR) data of the laundry at 460nm is presented in Table 4-11. Data for the *C_8/C_{12}ESO-mix* containing formulation was normalized to *NPE9* as shown in Figure 4-5 to compare performance between the two surfactants.

Table 4-11 Laundry performance (reflectance improvement at 460nm) of *C_8/C_{12}ESO-mix* comparing to *NPE9*

Sample Soil Name	***NPE9***	***C8/C12ESO-mix***
Blood/milk/ink on cotton	8.5±1.1	8.2±0.9
Tea on cotton	1.4±0.4	1.3±0.4
Coffee on cotton	2.6±0.4	3.6±0.4
Grass on cotton	18.8±1.9	19.7±2.8
Wine on cotton	14.9±0.8	15.3±0.6
Lipstick on cotton	13.5±1.7	14.1±1.8
Chocolate drink on cotton	20.5±2.3	19.6±2.2
Blood/milk/ink on PE/C	8.6±0.7	6.1±0.7
Tea on PE/C	1.7±0.6	1.4±0.4
Coffee on PE/C	3.5±0.4	3.3±0.4
Grass on PE/C	20.1±1.1	20.7±1.4
Wine on PE/C	10.8±0.6	10.2±0.5
Lipstick on PE/C	8.4±1.4	6.3±0.7
Chocolate drink on PE/C	23.2±1.8	23.5±1.5
Average	**11.2±1.0**	**11.0±1.1**

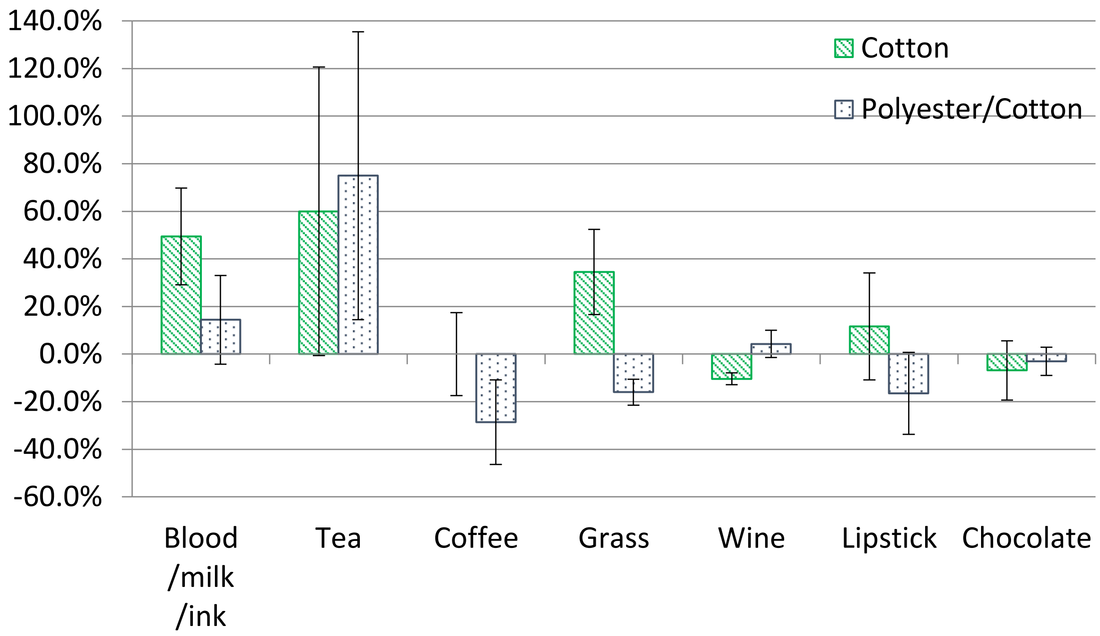


Figure 4-5 Laundry performance (reflectance improvement at 460nm) of *C_8/C_{12}ESO-mix* normalized to *NPE9*

Differences were apparent on some soil/fiber pairs of *C_8/C_{12}ESO-mix* and *NPE9*, but on the average, there was essentially no statistical deviation between the performances of the two surfactants. In other words, *C_8/C_{12}ESO-mix* was a good replacement for *NPE9* based on laundry performance data in an enzyme-containing formulation.

4.9 Summary

Sulfoxide-based nonionic surfactants derived from 2-hydroxy-4-(methylthio) butyric acid were highly surface active and can be water soluble at room temperature. Unique properties, such as very high cloud temperature, very low surface tension at the CMC, and very low surface area at the solution-air interface were found. These surfactants have good wetting kinetics and their foams dissipate faster than a nonyl-phenol ethoxylate surfactant. These surfactants were synergistic with sodium dodecyl sulfate at the same level with other nonionic surfactants as determined by surface tension measurements. In laundry testing, the performance of the formulation with one of these surfactants was on the average identical to the same formulation with nonyl-phenol ethoxylate surfactant instead.

Chapter 5 Nonionic Surfactants with Enhanced Headgroup Hydrophilicity

5.1 Surfactants

5.1.1 Nomenclatures

Schematic structures of 2-hydroxy-4-(methylthio) butyric acid, monomer ester sulfoxides (C_nESO), oligomer ester sulfoxides (C_nESO_m), ethoxylated ester sulfides (C_nEO_mES) and ethoxylated ester sulfoxides (C_nEO_mESO) are shown in Figure 5-1.

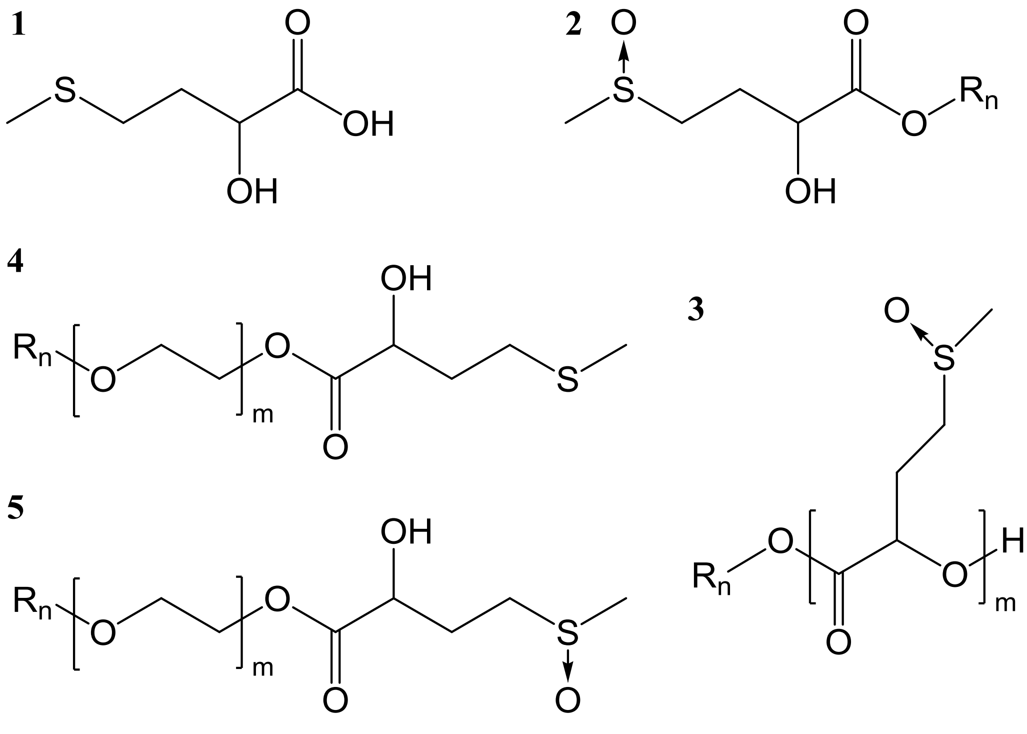


Figure 5-1 Structural comparison of 1. 2-hydroxy-4-(methylthio) butyric acid, 2. monomer ester sulfoxides (C_nESO), 3. oligomer ester sulfoxide (C_nESO_m), 4. ethoxylated ester sulfides (*C_nEO_mES*) and 5. ethoxylated ester sulfoxides (*C_nEO_mESO*)

The samples are abbreviated so that the name represents all the functional groups in the surfactant structure. For example, *$C_{12}EO_4ESO$* (3,6,9,12-tetraoxatetracosyl 2-hydroxy-4-(methylsulfinyl)butanoate) represents the ester of 2-hydroxy-4-(methylthio) butyric acid reacted with a commercial AE surfactant, tetraoxyethylene lauryl ether, which contains a dodecyl chain (C_{12}), an oligomer with 4 repeating ethylene oxide units (EO_4) followed by partial oxidation of the sulfide moiety. Compounds that consist of essentially more than one molecule, for example, ethoxylated ester sulfoxides (*C_nEO_mESO*), are italicized to distinguish from the compounds that contain a significant distribution of species, for example, all ethoxylated materials.

5.1.2 HPLC

The HPLC were performed in an Agilent 1260 system with acetonitrile as solvent and Dionex Acclaim® Organic Acid (OA 5µm, 120Å, 4 x 150mm) column. In order to confirm the purity of the dimer surfactants after the ion exchange chromatography, the surfactants were dissolved in water and analyzed by HPLC. The purity of the main components were characterized by the peak area.

Table 5-1 Purity of the nonionic surfactants determined by HPLC

Compound	HPLC purity by area %
$C_{12}ESO_2$	94.9
$C_{14}ESO_2$	98.3
$C_{16}ESO_2$	99.3
$C_{18}ESO_2$	99.5

Table 4-3 shows the HPLC determined purity of $C_{12}ESO_2$, $C_{14}ESO_2$, $C_{16}ESO_2$ and $C_{18}ESO_2$. All the surfactants presented purity level above 98%, except for $C_{12}ESO_2$ with a 94.9% purity.

5.2 Surface chemical properties

Surface tensions are plotted against surfactant concentration in water in Figure 5-2 and Figure 5-3. $C_{18}ESO_2$ was tested at 35˚C because of an upper critical solution temperature at 32˚C. Surface chemical properties of various surfactants, including CMC, surface tension at CMC (γ_{CMC}), pC20, CMC/C20, surface excess concentration (Γ_{max}) and minimum area per molecule at the interface (a_{min}), were calculated according to the γ vs. log C graphs and presented in Table 5-2.

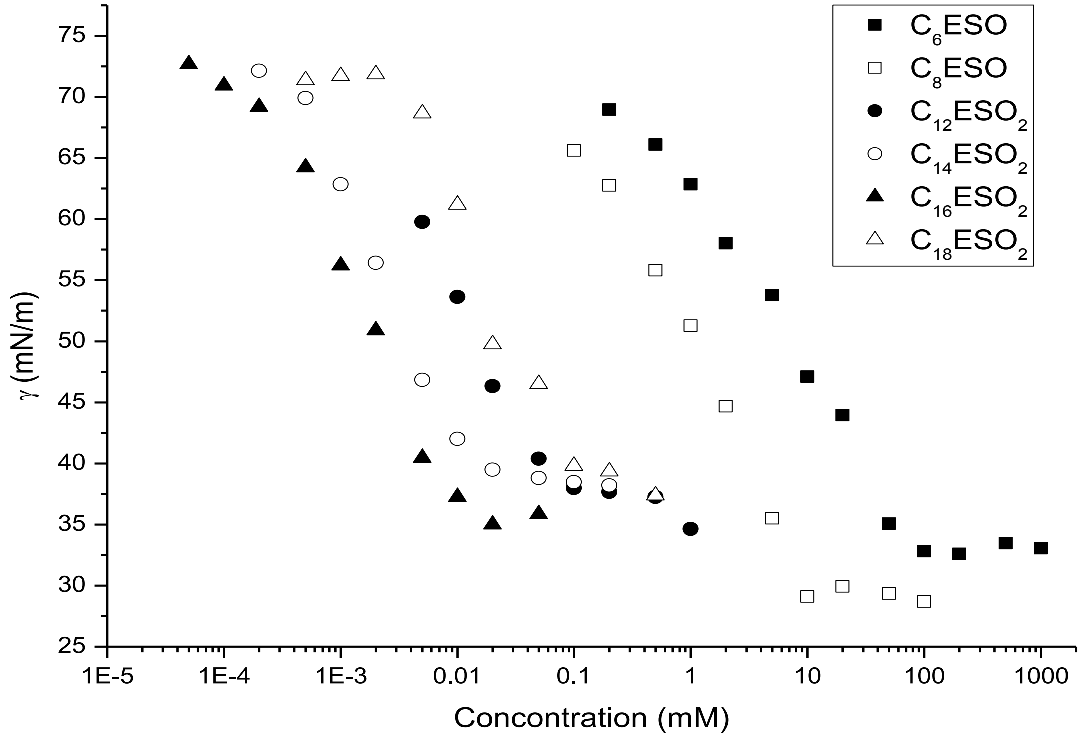


Figure 5-2 Surface tension measurements of monomer and dimer ester sulfoxides ($C_{18}ESO_2$ measured at 35˚C)

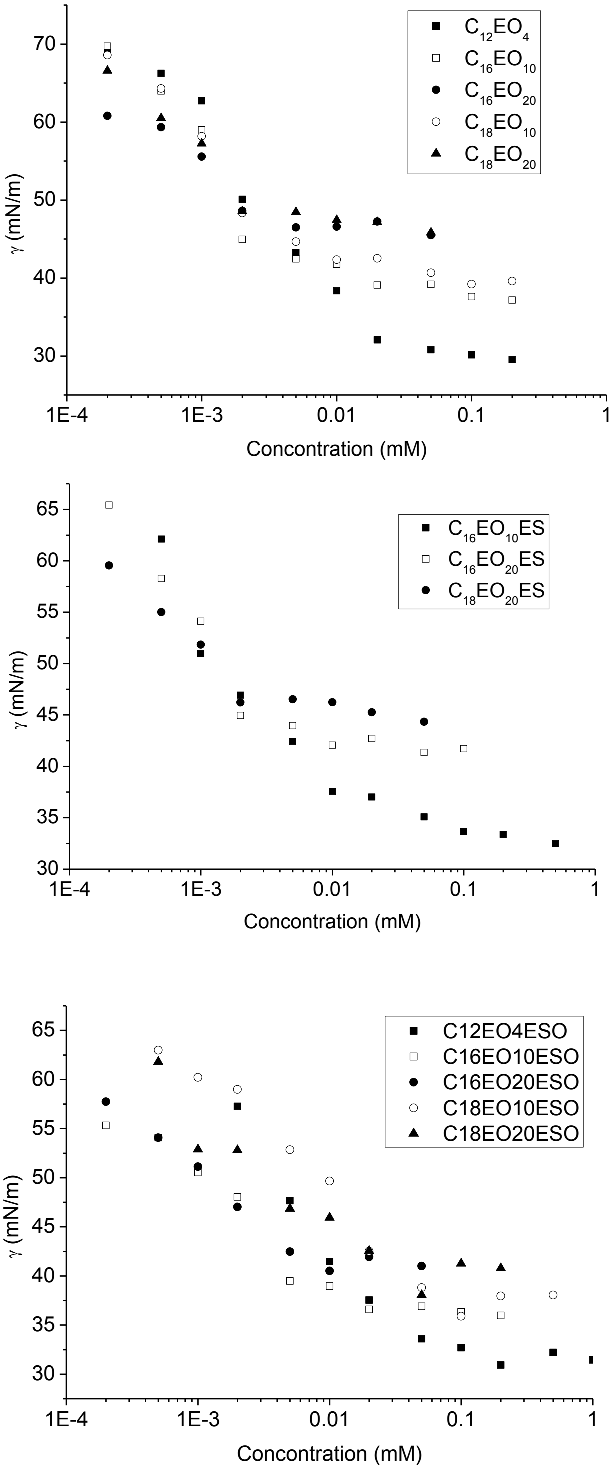


Figure 5-3 Surface tension measurements of ethoxylated ester sulfoxides/sulfides (C_nEO_mES/ C_nEO_mESO) and commercial ethoxylated alcohols (C_nEO_m)

Table 5-2 Surface chemical properties of monomer/dimer ester sulfoxides, ethoxylated ester sulfides/sulfoxides and commercial nonionic surfactants

Sample	**CMC (mM)**	**CMC (wt%)**	**γ_{CMC} (mN/m)**	**pC20**	**CMC/C20**	**Γ_{max} (mol/m^2)**	**a_{min} (Å^2)**
C_6ESO	104	2.6	33	2.4	23.9	2.5×10^{-10}	66.9
C_8ESO	11.7	0.33	29	3.2	17.5	3.3×10^{-10}	50.8
$C_{12}ESO_2$	0.050	0.0024	38	5.0	4.7	3.9×10^{-10}	42.4
$C_{14}ESO_2$	0.0083	0.00043	41	6.0	3.1	4.0×10^{-10}	41.3
$C_{16}ESO_2$	0.0073	0.00040	37	5.8	4.7	4.1×10^{-10}	40.7
$C_{18}ESO_2$ (35˚C)	0.023	0.0013	41	6.0	2.6	4.7×10^{-10}	35.6
$C_{12}EO_4$	0.018	0.00065	32	5.7	8.3	3.9×10^{-10}	43.1
$C_{12}EO_4ESO$	0.039	0.0020	33	5.5	11.7	3.2×10^{-10}	51.1
$C_{16}EO_{10}$	0.013	0.00092	41	5.6	5.4	2.8×10^{-10}	59.7
$C_{16}EO_{10}ES$	0.019	0.0015	37	6.0	14.4	2.3×10^{-10}	72.2
$C_{16}EO_{10}ESO$	0.029	0.0024	37	5.5	9.7	2.8×10^{-10}	59.9
$C_{16}EO_{20}$	0.0031	0.00035	48	5.8	2.1	2.4×10^{-10}	69.9
$C_{16}EO_{20}ES$	0.0057	0.00073	43	6.2	8.7	1.9×10^{-10}	89.5
$C_{16}EO_{20}ESO$	0.016	0.0021	41	5.8	2.8	2.1×10^{-10}	79.0
$C_{18}EO_{10}$	0.018	0.0013	40	5.6	7.4	2.6×10^{-10}	64.8
$C_{18}EO_{10}ESO$	0.020	0.0014	41	5.5	6.1	2.5×10^{-10}	67.0
$C_{18}EO_{20}$	0.0094	0.0011	46	5.6	3.3	2.0×10^{-10}	82.6
$C_{18}EO_{20}ES$	0.0086	0.0011	45	6.0	9.2	1.4×10^{-10}	115.2
$C_{18}EO_{20}ESO$	0.018	0.0024	42	5.7	8.9	1.9×10^{-10}	89.3
NPE9	0.038	0.0038	33	5.8	26.5	2.1×10^{-10}	79.4

The monomer and dimer sulfoxides followed Traube's rule[49] in that every two additional hydrocarbon units decrease the CMC or C20 by an order of magnitude. However, the CMC and C20 of dimer ester sulfoxide surfactants stops decreasing when C_{16} is reached (e.g. compare $C_{16}ESO_2$ and $C_{14}ESO_2$). Such result agrees with Greiss' results that when hydrocarbon chain length exceeds a certain value the CMC or C20 stops decreasing[56]; a later study attributed the behavior in linear alkane surfactants to hydrocarbon chains longer than 18 units starting to coil.[57] However, CMC and C20 of dimer ester sulfoxide surfactants stops decreasing at C_{16}, probably because these surfactants have some extra hydrocarbon units in the hydrophilic headgroup. The γ_{CMC}

of the dimer ester sulfoxides are larger than monomer ester sulfoxides, presumably because the large size of the dimer headgroup limits packing effectiveness at the water/air interface. The C_nESO_2 surfactants have very low CMC/C20, or high micelle formation tendency. The a_{min} of the dimers are quite low compared to the ethoxylated surfactants, suggesting that the dimer sulfoxides are still more compactly packed compared with the ethylene oxide oligomers.

CMCs of the ethoxylated ester sulfoxides are larger than the corresponding ethoxylated ester sulfides and alcohol ethoxylate surfactants because the additional sulfoxide group makes the molecules more hydrophilic. The difference is most considerable between $C_{12}EO_4ESO$ and $C_{12}EO_4$ compared to the other molecules in the current study, because, as the number of EO molecules increases, the addition of a sulfoxide has a lower relative impact on the hydrophilicity. Similar to C_nESO_2, the change from C_{16} to C_{18} has little effect on the CMC and pC20 for the ethoxylated ester sulfoxides. γ_{CMC} increases with the number of EO groups in C_nEO_mES, C_nEO_mESO and C_nEO_m, due to increased hydrophilic head group size. The CMC/C20 value, or the tendency of micelle formation decreased with increasing hydrocarbon number, or with decreasing number of EO groups in C_nEO_mES, C_nEO_mESO and C_nEO_m, which is probably because the shape of the surfactants became more favorable for spherical micelles. For C_nEO_mES, C_nEO_mESO and C_nEO_m, Γ_m decreased while the number of EO groups increased, because of the increased hydrophile size. As a result, a_{min} increased with increasing EO number.

5.3 Upper and lower critical solution temperatures

The upper critical solution temperature (UCST) and the lower critical solution temperature (LCST) of 1.0 wt% water solutions of the C_nESO, C_nESO_2 and C_nEO_mESO are presented in Table 5-3 in comparison with commercial AE surfactants, *NPE9* and SDS.

Table 5-3 LCST/UCST of 1.0 wt% aqueous solutions of ester sulfoxide monomers, dimers, ester sulfides/sulfoxides of ethoxylated alcohols and other nonionic surfactants

Samples (1.0 wt%)	**Lower critical solution temperature (°C)**	**Upper critical solution temperature (°C)**
C_6ESO	<4	>75
C_8ESO	<4	>75
$C_{12}ESO_2$	<4	>75
$C_{14}ESO_2$	<4	>75
$C_{16}ESO_2$	21	>75
$C_{18}ESO_2$	32	>75
$C_{12}EO_4ES$	Insoluble	Insoluble
$C_{12}EO_4ESO$	<4	>75
$C_{12}EO_4$	<4	>75
$C_{16}EO_{10}ES$	23	40
$C_{16}EO_{10}ESO$	16	>75
$C_{16}EO_{10}$	42	55
$C_{16}EO_{20}ES$	<4	>75
$C_{16}EO_{20}ESO$	<4	>75
$C_{16}EO_{20}$	<4	>75
$C_{18}EO_{10}ES$	Insoluble	Insoluble
$C_{18}EO_{10}ESO$	<4	>75
$C_{18}EO_{10}$	49	61
$C_{18}EO_{20}ES$	<4	>75
$C_{18}EO_{20}ESO$	<4	>75
$C_{18}EO_{20}$	<4	>75
Sodium Dodecyl Sulfate	22	N/A
NPE9	<4	53

The monomer and dimer ester sulfoxide surfactants with hydrophobes below hexadecyl do not have measurable UCST/LCST between 4˚C and 75˚C. $C_{16}ESO_2$ and $C_{18}ESO_2$ presented UCST at 21˚C and 32˚C, respectively. Longer hydrocarbon chains lead to higher UCST because of stronger hydrophobicity. $C_{16}EO_{10}$ and its corresponding ester sulfides/sulfoxides have UCST of 42˚C, 26˚C and 16˚C, respectively. $C_{18}EO_{10}$ presented UCST of 49˚C, but $C_{18}EO_{10}ESO$ has no observable UCST above 4˚C. The ester sulfoxide/sulfide groups lowered the UCST probably because these groups introduced a branch into the headgroup structure and made the formation of a surfactant-rich phase less desirable. The LCST, or the cloud temperature, is related to the weakening of hydrogen bonds from increased temperatures. Two commercial AE surfactants, $C_{16}EO_{10}$ and $C_{18}EO_{10}$ had LCST below 75˚C. The C_nEO_mES generally have lower LCST than their corresponding AEs, indicating that the ester sulfide group lowers the average hydrogen bonding tendency of the molecules. In other words, ester sulfide groups are more hydrophobic than the EO group. The corresponding C_nEO_mESO surfactants, however, presented higher LCST, meaning these surfactants are more hydrophilic than molecules with just EO units, which is to be expected since the sulfoxide groups have very high hydrogen bonding tendency.[54]

5.4 Draves wetting test

Table 5-4 presents Draves wetting test results for C_nESO and C_nEO_mESO compared with *NPE9*.

Table 5-4 Draves wetting performance of ethoxylated ester sulfides/sulfoxides and other nonionic surfactants

Wetting agent	**t_{sink} (s) @ 0.50%**	**t_{sink} (s) @ 0.25%**	**t_{sink} (s) @ 0.10%**	**t_{sink} (s) @ 0.05%**	**γ_{CMC} (mN/m)**
C_8ESO	instant	5	>300	>300	29
NPE9	instant	7	12	30	33
$C_{12}EO_4ESO$	8	10	18	50	33
$C_{16}EO_{10}ESO$	110	98	>300	>300	37
$C_{16}EO_{10}ES$	46	56	124	>300	37
$C_{16}EO_{20}ESO$	>300	>300	>300	>300	43

The C_nEO_mES/C_nEO_mESO wetted the skeins slowly, except for $C_{12}EO_4ESO$ which has a comparable wetting kinetics with *NPE9*. The wetting performance of these surfactants at 0.50 or 0.25 wt% correlated with their surface tension at the CMC very well; a lower surface tension yielded faster wetting kinetics. The molecular weight of the sulfoxide molecules are significantly larger than that of the NPE, which in turn should lead to a lower diffusion coefficient and slower wetting.

5.5 Foaming ability and stability profile

5.5.1 Ross-Miles foaming test

Ross-Miles foaming results of C_nESO and C_nEO_mESO at 1 wt% are presented in Figure 5-4, in comparison with *NPE9* and a commercial low-foaming alcohol alkoxylate surfactant (*AE-LF*).

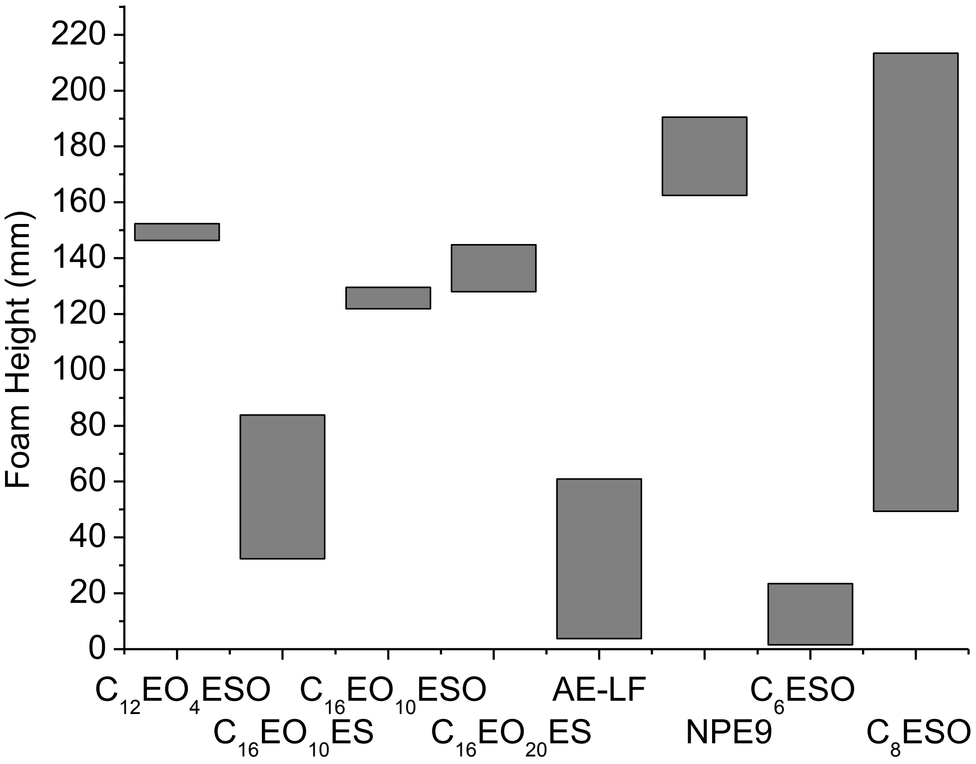


Figure 5-4 Ross-Miles foaming performance of ethoxylated ester sulfoxides/sulfides and monomer ester sulfoxides comparing with various nonionic surfactants (*AE-LF* is a low-foaming AE surfactant). The top of the bar represents foam height at time=0, while the bottom represents foam height at time=5 min.

NPE9 has the second highest initial foam and the highest foam after 5 min. AE-LF had a low initial foam (61mm) and minimal foam after 5 min (2mm). C_6ESO has very low initial foam (23mm) which completely disappeared after 5 min, probably because the surfactant concentration is below the CMC. *C_8ESO* created high foam initially, which dissipated very quickly, indicating a weakly packed surface monolayer. *$C_{12}EO_4ESO$*, *$C_{16}EO_{10}ESO$* and *$C_{16}EO_{20}ESO$* solutions created quite high and persistent foams, indicating that these surfactants forms quite cohesive surface. *$C_{16}EO_{10}ES$* created a small foam (84mm) which dissipated quite quickly within 5 min (32mm). The initial and dissipated foam of *$C_{16}EO_{10}ES$* is lower than all the surfactants except *AE-LF* and

C_6ESO. The comparison between C_nEO_mESO and C_nEO_mES suggests that ethoxylated ester sulfoxides created more cohesive surface than ethoxylated ester sulfides.

5.5.2 Foam collapse profile

The foaming ability of selected surfactants was further studied with foam collapse profile. Figure 5-5 shows the foam collapse profile of 1.0 wt% surfactant water solutions. Foam collapse profiles were fitted with the model described in the experimental section, and the parameters are presented in Table 5-5.

Table 5-5 Parameters of the foam collapse profile of various C_nEO_mES, C_nEO_mESO and C_nEO_m in comparison with two nonionic surfactants

Surfactants (1.0 wt%)	C_A (Diffusion)	K_A ($\times 10^{-3}$ s^{-1}) (Diffusion)	C_B (Draining)	K_B (s^{-1}) (Draining)
$C_{12}EO_4ESO$	0.50	0.23	0.50	0.13
$C_{16}EO_{10}ES$	0.57	1.2	0.43	0.22
$C_{16}EO_{10}ESO$	0.54	0.11	0.46	0.16
$C_{16}EO_{20}$	0.56	0.16	0.44	0.16
$C_{16}EO_{20}ES$	0.56	0.85	0.44	0.16
$C_{16}EO_{20}ESO$	0.56	0.13	0.44	0.15
AE-LF	0.92	53	0.08	0.15
NPE9	0.53	0.18	0.47	0.18

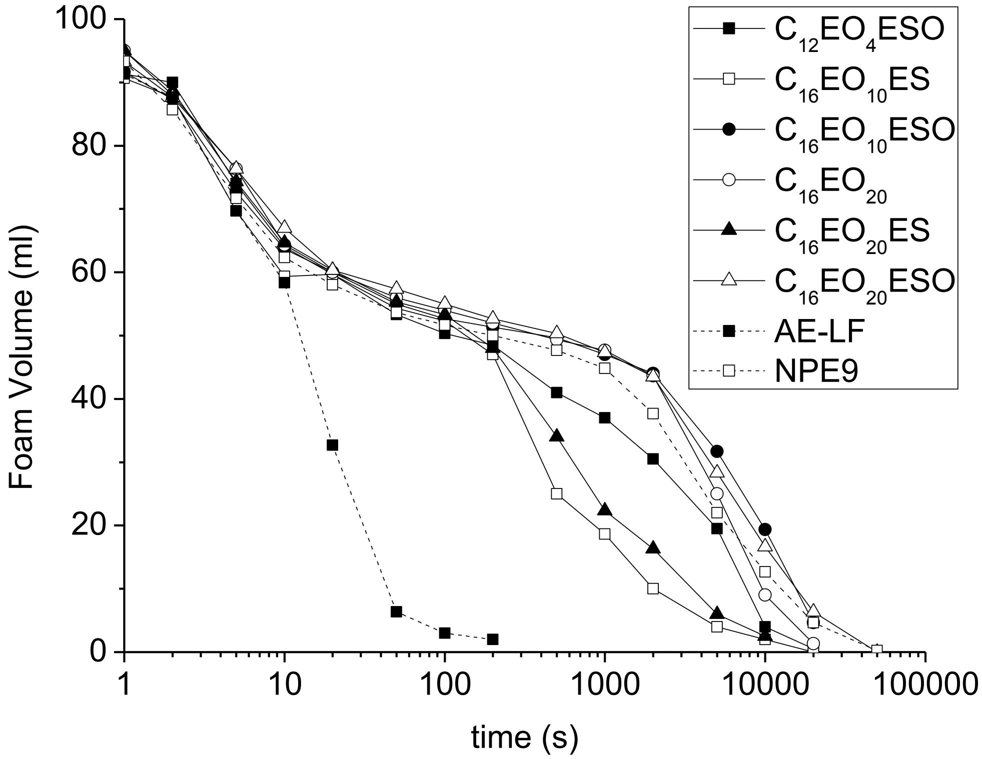


Figure 5-5 Foam collapse profile in the foam of 1.0 wt% water solutions of various *C_nEO_mES*, *C_nEO_mESO* and *C_nEO_m* in comparison with two nonionic surfactants (*AE-LF* and *NPE9*)

The foams decreased in height rapidly in the first 10s due to liquid drainage which then slowed down. Then the foams dissipates slowly because of gas diffusion through lamellae. All the foam draining profiles in the initial 10s coincided, except for *$C_{16}EO_{10}ES$* and *AE-LF*. These two surfactants presented the fastest diffusion in their foams, which may became significant in the initial 10s while the rest of the samples still had little or no diffusion.

Air diffusion occurred the fastest within *AE-LF*, *$C_{16}EO_{10}ES$* and *$C_{16}EO_{20}ES$* foams than the others. The *AE-LF* diffusion was the fastest. In general, the collapsing rate of the eight foams goes in the order: *AE-LF* > *$C_{16}EO_{10}ES$* > *$C_{16}EO_{20}ES$* > *$C_{12}EO_4ESO$* >

$NPE9 > C_{16}EO_{20} > C_{16}EO_{20}ESO \approx C_{16}EO_{10}ESO$, which is reflected by K_A or the air diffusion rate. AE-LF presented the fastest dissipating foam. The permeability to air of the lamellae is correlated with the arrangement of the surface monolayer and the thickness of the lamellae. Therefore, the longer the hydrophobes are, the slower the C_nEO_mESO foams collapsed. Another reason for *AE-LF* to have very unstable foam is that its cloud point is below room temperature (16-21˚C), and the separated surfactant phase can perform as a foam breaker.

Another observation is that the C_nEO_mES foams presented much higher diffusion rate than C_nEO_mESO, C_nEO_m and *NPE9*. In contrast to the traditional lipophilic-hydrophilic surfactants, these lipophilic-hydrophilic-lipophilic (LHL) or hydrophilic-lipophilic-hydrophilic (HLH) molecules occupy a larger area at the surface and form an incoherent film, as illustrated in Figure 5-6. Similar low-foaming polymers have been reported previously.[58]

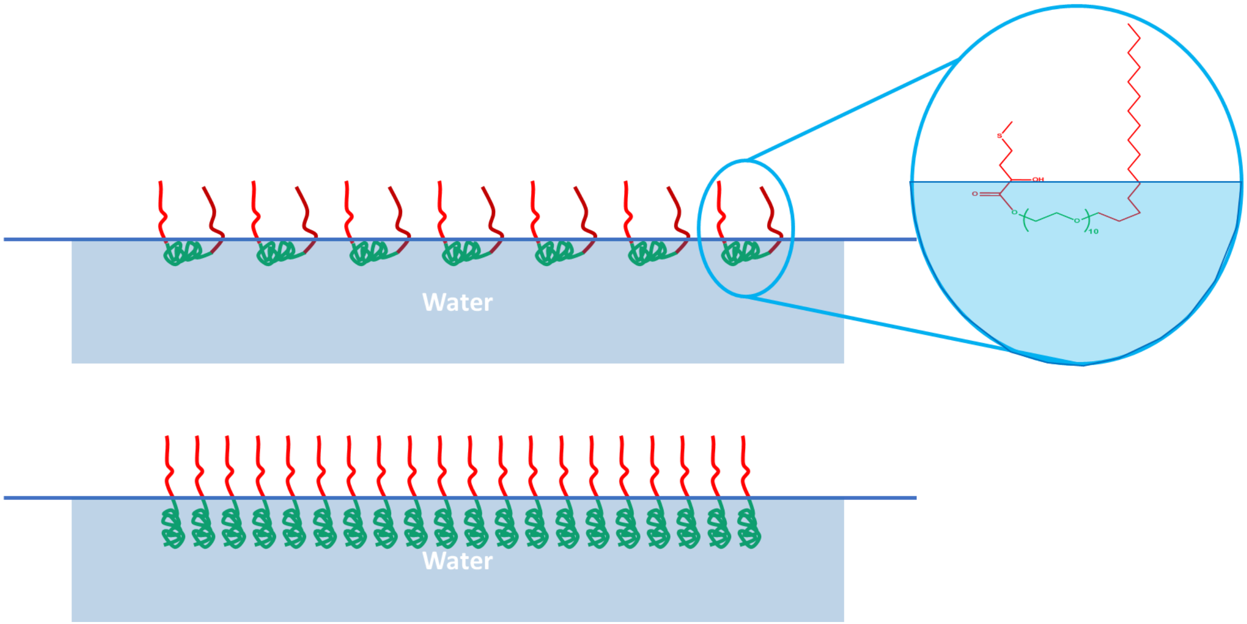


Figure 5-6 Illustration of proposed surface arrangement with higher surface area of LHL surfactant (top) and conventional LH surfactants (bottom), with the unoxidized *C_nEO_mES* (*$C_{16}EO_{10}ES$*) structure in the zoom-in

The *C_nEO_mES* molecules are LHL type structures because the unoxidized methylthio-butyl (S) group is hydrophobic. During the previous studies, we found that unoxidized sulfide ester had much lower solubility than sulfoxides. Hence, the ES groups in the *C_nEO_mES* surfactants prefer to reside in the hydrophobic phase causing an LHL structural form and hence fast gas diffusion.

5.6 Laundry performance

The formulation given in Table 2-1 was used to determine the performance of the nonionic surfactants as the nonionic component of a standard laundry formulation with enzymes and flourescers. Our concern was that the sulfoxide might affect the efficacy of these agents so we wanted to be sure to include those in the formulation.

Table 5-6 presents the reflectance improvement (ΔR) at 460 nm as the laundry efficiency data of the soiled fabrics washed with the formula containing $C_{12}EO_4ESO$ or *NPE9*. The laundry efficiency data in Table 5-6 of $C_{12}EO_4ESO$ were normalized against *NPE9* and presented in Figure 5-7.

Comparing to *NPE9*, $C_{12}EO_4ESO$ performed better on blood/milk/ink, tea and lipstick (only on cotton), less efficient on coffee, and within statistical error on other soils. On average, $C_{12}EO_4ESO$ and *NPE9* performed equally well statistically.

Table 5-6 Laundry performance of $C_{12}EO_4ESO$ compared with *NPE9*

Soil Sample Name	**Reflectance Improvement (ΔR)**	
	NPE9	**$C_{12}EO_4ESO$**
Blood/milk/ink on cotton	9.3±1.1	15.7±2.0
Tea on cotton	1.0±0.4	1.3±0.6
Coffee on cotton	3.0±0.6	1.7±0.4
Grass on cotton	18.8±2.7	17.9±2.5
Wine on cotton	24.1±0.6	19.7±0.7
Lipstick on cotton	13.8±1.8	18.1±2.8
Chocolate drink on cotton	20.5±2.3	20.0±1.9
Blood/milk/ink on PE/C	11.1±1.0	15.2±2.9
Tea on PE/C	2.0±0.7	3.3±1.6
Coffee on PE/C	4.9±0.9	2.6±0.6
Grass on PE/C	26.3±1.7	25.8±1.8
Wine on PE/C	18.6±0.9	17.7±0.8
Lipstick on PE/C	8.5±2.1	8.3±1.2
Chocolate drink on PE/C	29.2±1.9	25.8±2.8
Average	**13.7±1.5**	**13.8±1.8**

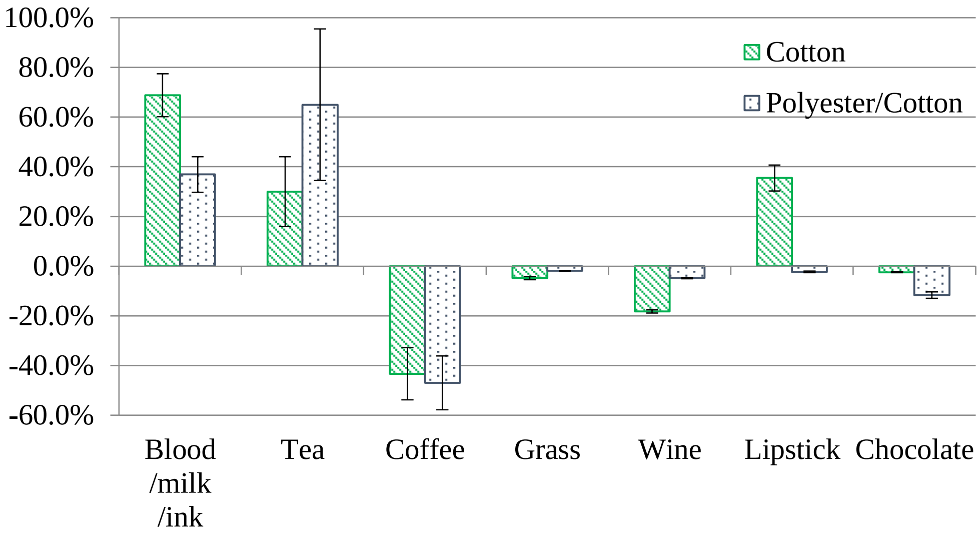


Figure 5-7 Laundry performance of *$C_{12}EO_4ESO$* normalized to *NPE9*

5.7 Summary

Sulfoxide/sulfide-based surfactants were synthesized from 2-hydroxy-4-(methylthio) butyric acid with an oligomeric headgroup or in combination with EO groups. C_nESO_2 surfactants have high water solubility, very low CMC and low surface tension at CMC, and low surface area at the water-air interface. C_nEO_mESO have good water solubility, low CMC, and good Draves wetting kinetics. C_nEO_mES solutions made foams which dissipated very fast. In an enzyme-containing laundry formulation, the performance of the formulation containing $C_{12}EO_4ESO$ as the nonionic surfactant was statistically the same to the performance of the formulation containing a commercial nonyl-phenol ethoxylate surfactant.

Chapter 6 Microemulsions Based on Sulfoxide Surfactants

6.1 Phase behavior

Phase transition temperatures ($T_{I/III}$ and $T_{III/II}$) of the sulfoxide surfactants/water/oil systems are presented in Table 6-1. Please note that the EACN for the aromatic oils and the cyclic alkanes are obtained from previous microemulsion studies, and the apparent EACN values of these oils may vary with different surfactants.[21]

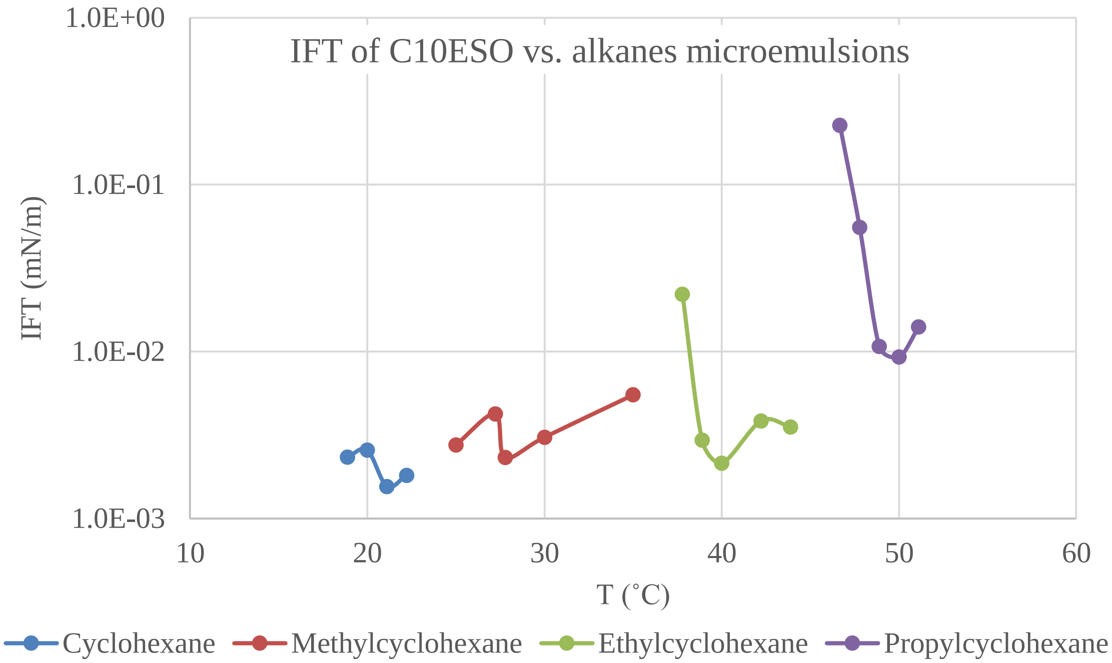
Table 6-1 $T_{I/III}$ and $T_{III/II}$ of C_nESO with various oils

Surfactants	Oils	EACN	$T_{I/III}$ (˚C)	$T_{III/II}$ (˚C)
C_8ESO (3%)	Xylenes	1~2	<0	1
C_8ESO (3%)	Trimethylbezene	1~3	<0	34
C_8ESO (3%)	Diethylbenzene	2~4	25	74
C_8ESO (3%)	Cyclohexane	2.2[59]	49	>80
$C_{10}ESO$ (3%)	Diethylbenzene	2~4	<0	6
$C_{10}ESO$ (3%)	Cyclohexane	2.2	14	25
$C_{10}ESO$ (2%)	Methylcyclohexane	3.2[59]	20	70
$C_{10}ESO$ (2%)	Ethylcyclohexane	3.8[60]	29	>80
$C_{10}ESO$ (2%)	Propylcyclohexane	5.6[60]	45	>80
$C_{10}ESO$ (5%)	n-Hexane	6	37	>80
$C_{10}ESO$ (5%)	n-Heptane	7	45	>80
$C_{10}ESO$ (3%)	n-Octane	8	48	>80
$C_{12}ESO$ (1%)	n-Hexane	6	14	16
$C_{12}ESO$ (1%)	n-Heptane	7	18	22
$C_{12}ESO$ (1%)	n-Octane	8	28	31
$C_{12}ESO$ (1%)	n-Nonane	9	30	36
$C_{12}ESO$ (1%)	n-Decane	10	41	46

Type III microemulsions are formed with these systems within the temperature range of 0-80˚C. The $T_{I/III}$ and $T_{III/II}$ increase with reducing surfactant hydrophobe length and increasing EACN of oils. The sulfoxide surfactants behave similarly to nonionic surfactants because the emulsion phase behaviors are sensitive to temperature. Most of the $T_{I/III}$ and $T_{III/II}$ are within the measurable range of 0-80˚C, but some of the emulsions do not see phase transitions within this range. These data cannot precisely determine the PITs because a. the determination of $T_{I/III}$ and $T_{III/II}$ is based on visual observation, and b. it is impossible to obtain the middle point of $T_{I/III}$ and $T_{III/II}$ if $T_{I/III}$ or $T_{III/II}$ is outside the measurement range.

6.2Interfacial tension

The oil/water IFT vs. temperature curves of C_{10}ESO/C_{12}ESO-alkanes are presented in Figure 6-1. All curves showed concave shapes with a minimum IFT at the PIT. PITs and the minimum IFTs of these microemulsions are presented in Table 6-2. The IFT of these systems are in the ultralow range ($<10^{-2}$mN/m), therefore having very high solubilization ratio according to Chun Huh relationship[31]. PITs increase with increasing EACN for both C_{10}ESO and C_{12}ESO microemulsions. Comparing to C_{12}ESO, C_{10}ESO was able to emulsify oils with lower EACN with a similar PIT (C_{12}ESO/n-octane vs. C_{10}ESO/methylcyclohexane), which means that PIT decrease with increasing hydrophobe size of the surfactant. The change of PIT with varied hydrophobe length and EACN agreed with the behaviors of EO-type nonionic surfactants in microemulsions.[17-18]



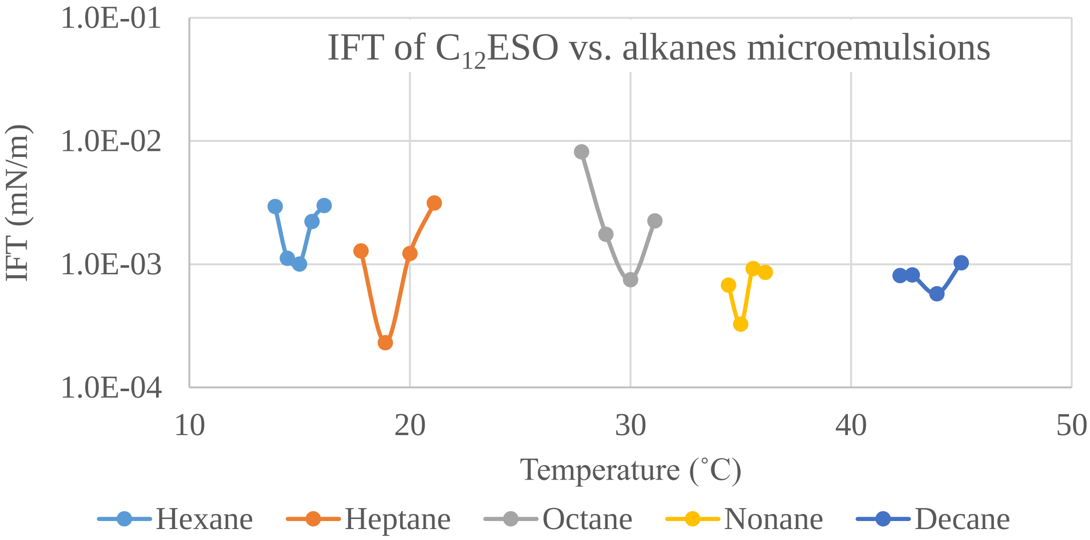


Figure 6-1 IFT vs. temperature graphs of C_{10}ESO (top) and C_{12}ESO (bottom) with various alkanes

Table 6-2 PITs and minimum IFTs of C_{12}ESO with various alkanes

Surfactants	**Oils**	**EACN**	**PIT (˚C)**	**IFT_{min} (mN/m)**
C_{10}ESO	Cyclohexane	2.2	21.1	1.6×10^{-3}
C_{10}ESO	Methylcyclohexane	3.2	27.8	2.3×10^{-3}
C_{10}ESO	Ethylcyclohexane	3.8	40	2.1×10^{-3}
C_{10}ESO	Propylcyclohexane	5.6	50	9.3×10^{-3}
C_{12}ESO	n-Hexane	6	15.0	1.0×10^{-3}
C_{12}ESO	n-Heptane	7	18.9	2.3×10^{-4}
C_{12}ESO	n-Octane	8	30.0	7.5×10^{-4}
C_{12}ESO	n-Nonane	9	35.0	3.3×10^{-4}
C_{12}ESO	n-Decane	10	43.9	5.8×10^{-4}

6.3HLD model parameters

6.3.1 Parameters from PIT vs. EACN scan

When S=0 and f(A)=0, the HLD model presented in Chapter 2 was simplified to obtain:

$$EACN = {}^{c_T}/_{K} \cdot (PIT - 25) + {}^{\sigma}/_{K} \qquad \text{Equation 6-1}$$

Therefore, by doing a simple linear regression of the PIT vs. EACN data, one can obtain the HLD parameters c_T/K and σ/K. Hence, PIT vs. EACN data C_{10}ESO and C_{12}ESO in comparison with various AE surfactants by Sottman and Strey[17] are fitted with lines as presented in Figure 6-2.

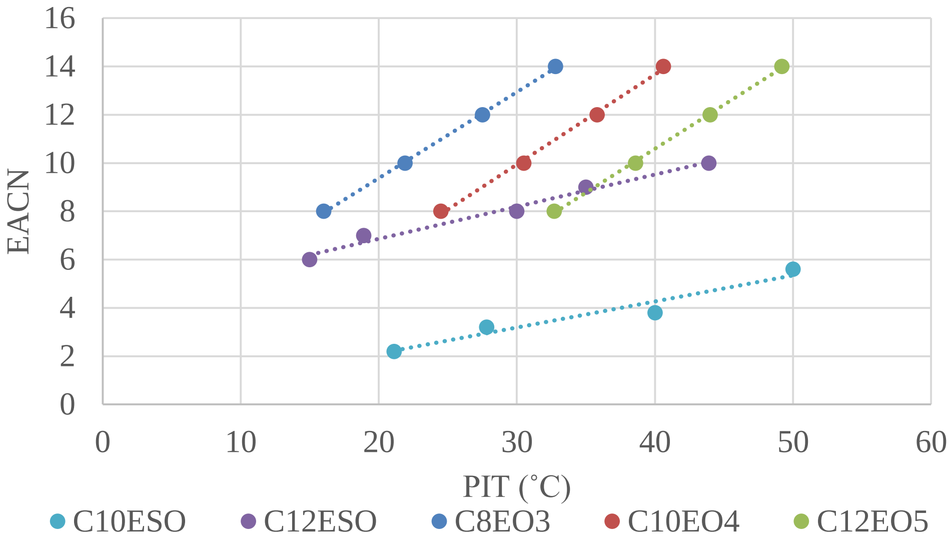


Figure 6-2 EACN vs. PIT curves for C_{10}ESO and C_{12}ESO in comparison with various AE surfactants by Sottman and Strey

From the linear regression, the value of c_T/K and σ/K of C_{10}ESO and C_{12}ESO can be obtained, as presented in Table 6-3, in comparison with AE surfactants.

Both the sulfoxide surfactants presented lower c_T/K than the AE surfactants, which means their PITs are more sensitive to a change in EACN. However, the temperature sensitivity of the surfactants cannot be determined, since the K parameter might be the source of the sensitivity of PIT to EACN. σ/K has been termed the "optimum EACN", the optimum EACN is the EACN of the oil that forms an optimum microemulsion with the lowest IFT with this surfactant at T=25˚C in pure water. Further, Salager reported that for EO-type nonionic surfactants, $\partial(\sigma/K)/\partial N_{C,S} = 2.25$; for sulfoxides, this number is 2.44, which is quite close to those of EO-type surfactants.

Table 6-3 HLD parameters of $C_{10}ESO$ and $C_{12}ESO$ compared with three AE surfactants[17]

Surfactants	c_T/K	σ/K
$C_{10}ESO$	0.11	2.6
$C_{12}ESO$	0.13	7.5
C_8EO_3	0.36	11.2
$C_{10}EO_4$	0.37	8.1
$C_{12}EO_5$	0.36	5.1

6.3.2 K parameter

The following equation is true assuming K is constant for a surfactant class:

$$K = \frac{\partial\sigma / \partial N_{C,S}}{\partial(\sigma/K) / \partial N_{C,S}} \qquad \text{Equation 6-2}$$

Equation 2-11 gives the value of the numerator in Equation 6-2 equal to 0.28 for hydrocarbon based nonionic surfactants. Assuming this value is the same for sulfoxide surfactants, then K of sulfoxide based surfactants and alkanes systems is equal to 0.28/2.44=0.11, and hence the values of c_T and σ can be calculated, as presented in Table 6-4 ($K_{AEs}=0.17$[35]). The emulsion temperature sensitivity is a measure of how much temperature needs to be changed in order to adjust for a change in oil hydrophobicity, a lower temperature sensitivity means more temperature change is needed for a given change in hydrophobicity. The emulsion temperature sensitivity (c_T) of the sulfoxide surfactants is significantly lower than that of the AE surfactants, which is in compliance with the high cloud temperature of this surfactant family, possibly because of the strong hydrogen bonding of the sulfoxide group with water. Based on σ, the indicator of surfactant hydrophobicity at 25˚C with no added salt, $C_{12}ESO$ ($\sigma=0.86$)

is almost equally hydrophobic to $C_{12}EO_5$ (σ=0.87), indicating that 1 ester sulfoxide (ESO) unit is as hydrophilic as 5 EO groups. Similar comparison can be done between $C_{10}ESO$ (σ=0.30) and $C_{10}EO_4$ (σ=1.4), that 1 ester sulfoxide (ESO) unit is more hydrophilic than 4 EO groups.

Table 6-4 c_T and σ of $C_{10}ESO$ and $C_{12}ESO$ compared with three AE surfactants[17]

Surfactants	**c_T**	**σ**
$C_{10}ESO$	0.012	0.30
$C_{12}ESO$	0.015	0.86
C_8EO_3	0.061	1.9
$C_{10}EO_4$	0.063	1.4
$C_{12}EO_5$	0.061	0.87

6.4Summary

Middle phase microemulsions were produced with water solutions of sulfoxide based surfactants and hydrocarbon oils without added salt. The PITs were screened with temperature scan of phase behaviors and determined with IFT measurements. Ultralow water/oil IFT as low as 10^{-4}mN/m were obtained with such systems. The PIT data were fitted with the HLD model to obtain the parameters such as characteristic curvature and temperature sensitivity. Based on microemulsion behavior, 1 sulfoxide ester moiety was found to be equally hydrophilic as 5 EO groups.

Chapter 7 Conclusions and Future Work

7.1Hydrophilicity of the Sulfoxide Ester Units

Hydrophilicity of a headgroup unit can be determined from its effect on the surfactant properties, such as CMC, solubility, cloud point, and microemulsion test. An interesting question for the researchers is how many equivalent EO groups is one ESO group in terms of hydrophilicity. At the end of Chapter 6, the hydrophilicity of the ESO unit was discussed according to the microemulsion studies. It was found that each ESO unit is as hydrophilic as 5 EO groups in AE surfactants in terms of microemulsion behavior. The CMC, solubility and cloud point of the sulfoxide based surfactants are summarized and compared to AE surfactants in Table 7-1. The CMCs seem to be varying significantly with hydrophobes, and very slightly with number of EO groups in the headgroup. Therefore, CMC is not a good variable for comparing the hydrophilicity of ESO and EO. Cloud point, on the other hand, presented a much more obvious change with the number of EO groups. C_6ESO has a cloud point higher than C_6EO_5 and C_8ESO has a cloud point higher than C_8EO_6. When comparing the ESO dimers, $C_{16}ESO_2$ presented higher cloud point than $C_{16}EO_8$, and possibly than $C_{16}EO_{12}$, too. What is quite the contrary is that $C_{10}ESO$ and $C_{12}ESO$ presented lower cloud point than $C_{10}EO_4$ and $C_{10}EO_4$, respectively. As discussed in Chapter 4, cloud point is not only affected by the hydrophilicity, but also by the shape of the molecules, which is the possibly the reason for the sudden drop of cloud point from C_8ESO to $C_{10}ESO$. In summary, based on cloud point, one ESO group is as hydrophilic as 3-6 EO groups, which agrees with the microemulsion results.

Table 7-1 CMC and cloud point of monomer/dimer ester sulfoxides and ethoxylated alcohols

Sample	CMC (mM)	Cloud Point (˚C)
C_{6}ESO	104	>75
C_{8}ESO	11.7	>75
C_{10}ESO	0.59*	<4
C_{12}ESO	0.060*	<4
$C_{12}ESO_{2}$	0.050	>75
$C_{14}ESO_{2}$	0.0083	>75
$C_{16}ESO_{2}$	0.0073	>75
$C_{6}EO_{3}$	90[61]	37[62]
$C_{6}EO_{5}$	90[61]	75[62]
$C_{6}EO_{6}$	70[63]	83[62]
$C_{8}EO_{4}$	8[63]	35.5[62]
$C_{8}EO_{6}$	9.9[61]	68[64]
$C_{10}EO_{4}$	0.68[65]	21[66]
$C_{10}EO_{5}$	0.76[67]	44[66]
$C_{10}EO_{6}$	0.90[61]	60[62]
$C_{12}EO_{4}$	0.064[48]	4[66]
$C_{12}EO_{5}$	0.064[48]	27[66]
$C_{12}EO_{6}$	0.087[61]	52[68]
$C_{12}EO_{7}$	0.082[48]	62[68]
$C_{12}EO_{8}$	0.11[48]	79[62]
$C_{12}EO_{10}$	0.09[63]	95[62]
$C_{14}EO_{6}$	0.010[61]	45[62]
$C_{16}EO_{6}$	0.0017[61]	32[62]
$C_{16}EO_{8}$		63[66]
$C_{16}EO_{12}$		92[66]

7.2Conclusions

The pursuit of quality in life is an ever-lasting aspiration of efforts to improve human knowledge. In this dissertation, we have seen attempts and successes to cater to such needs. The anionic surfactants provided an excellent alternative to sulfate soaps because both have high hardness tolerance. The sulfoxide nonionic surfactants were the outcome of a carefully engineered design to replace a product that is being removed from the market. Higher amphiphilicity was added to match the broad spectrum of surface active additive consumer demands.

Anionic surfactants derived from 2-hydroxy-4-(methylthio) butyric acid are hardness tolerating compounds with significant surface activity. High surface tension reduction and low CMC make these chemicals economical anionic surfactants. Their good solubility and low crystallization tendency is another advantage over conventional sulfates. The unique fast foam dissipation of these compounds may offer them another market niche.

The sulfoxide esters/amides were targeted at replacing nonylphenol ethoxylates (NPE) in the laundry detergent market. Outstanding phase behavior in water solution was observed of the sulfoxides, such as total miscibility and high cloud points. In combination with anionic surfactants, sulfoxides have CMC with minimal dosage, resulting from their low CMC and high synergistic constant with the anionics. One sulfoxide compound shares similar performances with a typical commercial NPE on adsorption isotherm and foaming tests, and more importantly, laundry performance tests.

Sulfoxide surfactants with enhanced headgroup hydrophilicity include dimer sulfoxide esters and ethoxylated sulfoxide esters. The two classes are based on different schemes, but share one purpose, to contain more hydrocarbon units in a water-soluble molecule. Lower CMCs and hence formula costs are one of the resolutions of enhanced amphiphilicity. More importantly, a surfactant family with tunable hydrophilicity promises to fit variable scopes of surfactant applications.

More functions of the surfactants derived from 2-hydroxy-4-(methylthio) butyric acid were investigated. Ethoxylated sulfide esters presented quickly dissipating foams, useful in applications including automatic dish/laundry cleaning and metal processing. Microemulsions of alkanes and water were formed with sulfoxide esters. Ultralow IFT between excess water and oil phases was obtained in such emulsions. Phase inversion temperatures lower to marginally higher than room temperature make these emulsions convenient in applications such as enhance oil recovery and hard surface cleaning.

7.3Future Work

One has seen the potentials of the novel sulfoxide containing headgroups in this dissertation. Multiple research routes can be proposed to further understand the new headgroup units.

For application investigations, one reasonable plan is to carry out more tests to understand the microemulsion behavior of the sulfoxide surfactants. The sulfoxide microemulsion’s salinity sensitivity, their hydrolysis profiles and aqueous stability should be studied. It would also be interesting to study the mixture of sulfoxide nonionic surfactants and anionic emulsifiers, and see how the sulfoxides can affect the IFT of the anionic microemulsions.

The discussions of sulfoxide hydrophilicity in Chapter 6 and 7 raise another question; why are the sulfoxides so hydrophilic? One proposed explanation is the strong hydrogen-bonding tendency of the sulfoxides, but it would be an interesting research to confirm the hypothesis. Another interesting property of the sulfoxide surfactants is their γ_{CMC} in aqueous solutions as low as 27mN/m, indicating a very high adsorption density despite the branching in the sulfoxide ester headgroup. Raman spectrum and/or NMR may be good tools for such research.

One ever-suspending question about the sulfoxides is whether these groups are uncharged (nonionic) or charged (amphoteric, similar to amine oxides) in water solutions. If the sulfoxides are charged, then the surfactant properties (i.e., solubility, cloud point, CMC and/or adsorption) are likely reacting to pH change. Sulfoxide amides are good candidates for this study because of their tolerance to low/high pHs. Amphoteric surfactants are also probably more sensitive to salt concentration as well. Investigation of the sulfoxide-surfactant property change with varying salinity should also be interesting, i.e., CMC, liquid/solid adsorption, microemulsions, etc.

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