J Am Oil Chem Soc (2011) 88:1223–1228
DOI 10.1007/s11746-011-1784-1

ORIGINAL PAPER

Effect of Extended Surfactant Structure on Interfacial Tension and Microemulsion Formation with Triglycerides

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Received: 17 September 2010 / Revised: 4 February 2011 / Accepted: 9 February 2011 / Published online: 26 February 2011

Abstract In this work, the impacts of extended surfactant structure (number of polypropylene oxide PO groups and branching nature of the hydrocarbon chain) on microemulsion formation and IFT values were examined with triglyceride oils. The results show that branching of the hydrocarbon tail of extended surfactants lowers optimum salinity and IFT values. The results also show that for the surfactants studied ultralow IFTs and microemulsion formation with vegetable oils can be achieved using extended surfactants with at least eight PO groups.

Keywords Triglycerides · Vegetable oils · Microemulsion · Extended surfactant · Solubilization · Interfacial tension

Introduction

Triglycerides are the main components in vegetable oils, fish oils and algae oils. Traditionally, triglycerides have been used as important lipid sources in human diet and for cooking purposes [1]. Recently, triglycerides have been explored as environmental friendly and renewable materials in industrial processes and as natural ingredients in consumer products [2–6]. Microemulsions have many unique characteristics that can be exploited in new triglyceride applications. For example, triglyceride microemulsions can achieve low interfacial tension (IFT) which is essential in applications like oil and grease detergency or water-based extraction of triglycerides from oil seeds or algae [7, 8]. Other microemulsion characteristics, such as thermo-dynamical stability, transparency and high solubilization capacity, are required properties in applications such as biodiesel, cosmetic and pharmaceutical products. Therefore, triglyceride microemulsions are of special research interest.

Microemulsions are thermodynamically stable mixtures of oil and water produced using surfactant formulations [9]. Microemulsions have been thoroughly reviewed elsewhere [9–12]. In short, microemulsion systems can be classified into three categories known as Winsor Type I, II, III microemulsions. In Winsor Type I microemulsions, the oil is solubilized in normal micelles in the water phase. In Winsor Type II microemulsions, water is solubilized in reverse micelles in the oil phase. Winsor Type III microemulsions, sometimes referred to as middle phase microemulsions, can be envisioned as both water and oil swollen micelles in a bi-continuous structure [9]. With increasing hydrophobicity of the surfactant system (e.g. increasing salinity for anionic surfactant system), the microemulsion system transitions from Winsor Type I, to Type III and to Type II (Fig. 1) and the oil/water interfacial tension $IFT_{o/w}$ goes through a minimum value at optimum condition in Winsor Type III region. Salinity, IFT and solubilization parameter (volume of oil or water solubilized in microemulsion per mass of surfactant) at optimum conditions are denoted as S*, IFT* and SP*.

Despite extensive microemulsion work with *n*-alkane oils and chlorinated hydrocarbons, triglycerides remain the

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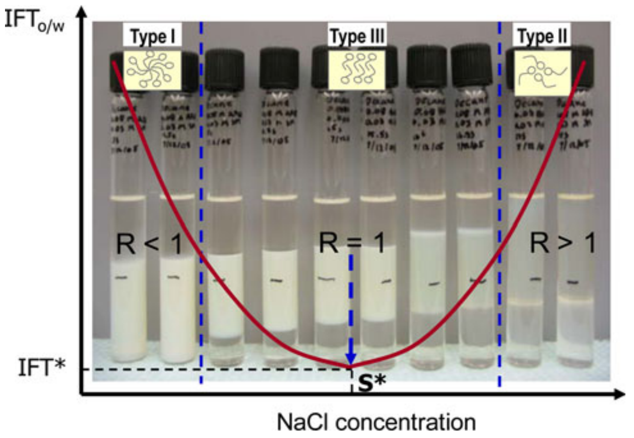


Fig. 1 Typical microemulsion phase transition and $IFT_{o/w}$ profile in a salinity scan of an anionic surfactant system

most challenging oil to microemulsify due to their unique structures. Triglycerides are esters of glycerol and three fatty acids, which may have the same or different alkyl lengths that can be saturated or unsaturated. The hydrocarbon chains of the fatty acids can be as long as 24 carbons [6]. Several researchers have reported triglyceride microemulsion formation using different approaches such as co-oil addition, alcohol addition, non-ionic surfactants at high temperature, and extended surfactants with linkers [13–23]. Among the published work on triglyceride microemulsions, the use of extended surfactant in triglyceride microemulsion [16, 22–25] has gained special interest because of the ability of extended surfactants to provide ultralow IFT and very high solubilization enhancement.

Extended surfactants were first introduced in 1995 by Minana-Perez et al. [16]. The concept of extended surfactants (Fig. 2) originated from the effort to increase the surfactant-oil interaction. Attempting to increase this interaction by increasing surfactant hydrocarbon chain length is limited to 18 or fewer carbons due to surfactant phase separation beyond that point. To overcome this limitation, polypropylene oxide (PO) groups, which have intermediate polarity, were inserted between the head group and the tail of the surfactant. The introduction of PO groups in the hydrophobe of the surfactant molecules helps to extend the tail further into the oil phase without sacrificing water solubility due to the longer tail. On the water side, the interactions with the water phase can be enhanced by inserting polyethyleneoxide (EO) groups. This arrangement is also believed to provide a smoother transition in polarity at the interface [9] which is considered a key factor in achieving high solubilization with highly hydrophobic oils (e.g. long chain hydrocarbons and triglycerides). Although previous work has demonstrated that extended surfactants can provide ultralow IFT and high solubilization capacity for triglyceride microemulsions [9, 16], limited information is available on how the structure of extended surfactant molecules affect their IFT values and their ability to form microemulsions with different triglyceride oils.

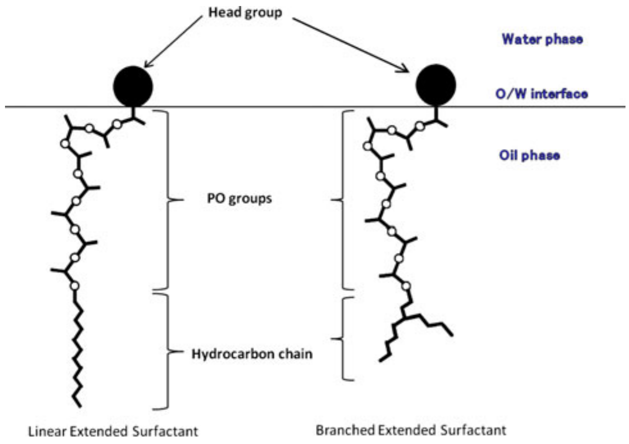


Fig. 2 Schematic of extended surfactant molecule configuration

This work evaluates the impact of extended surfactant structure (e.g. number of PO groups and branching nature of the hydrocarbon chain) on microemulsion phase behavior and IFT values with various triglyceride oils. Understanding these effects is of great importance for optimizing extended surfactant structures to deliver desired microemulsion properties for various triglyceride applications.

Methods

Materials

Extended surfactants used in this work are of the type sodium alkyl polypropylene oxide sulfate surfactants ($R–(PO)_x–SO_4Na$) and were provided by Sasol North American Inc. (Lake Charles, LA). Properties of the surfactants are summarized in Table 1. For the branched $R–(PO)_x–SO_4Na$ surfactants, the branched hydrocarbon tails were mixtures of possible branched isomers of the hydrocarbon chains. All extended surfactants were used as received.

Tricaprylin (C8:0) and canola oil were used in this work to represent short chain saturated triglycerides and long chain unsaturated triglycerides, respectively. Tricaprylin (99% purity) was purchased from Sigma Chemicals (St. Louis, MO). Canola oil was purchased from a local store. Sodium chloride (>99% purity) was purchased from Sigma-Aldrich (St. Louis, MO).

Methods

Phase behavior studies were conducted using salinity (NaCl) scans at different NaCl concentrations at an oil to

Table 1 Properties of extended surfactants

Nomenclature	Chemical formula	Degree of branching (%)	% active	Molecular weight (g/mol)
C123(B)–4PO–SO_4	$C_{12,13}H_{25,27}$–$(PO)_4$–SO_4Na	100	30.0	527
C123(B)–8PO–SO_4	$C_{12,13}H_{25,27}$–$(PO)_8$–SO_4Na	100	30.7	766
C145(B)–4PO–SO_4	$C_{14,15}H_{29,31}$–$(PO)_4$–SO_4Na	100	30.0	553
C145(B)–8PO–SO_4	$C_{14,15}H_{29,31}$–$(PO)_8$–SO_4Na	100	29.5	783
C123(L)–4PO–SO_4	$C_{12,13}H_{25,27}$–$(PO)_4$–SO_4Na	0	27.3	519
C123(L–B)B–4PO–SO_4	$C_{12,13}H_{25,27}$–$(PO)_4$–SO_4Na	50	28.1	527

water ratio of 1:1 and surfactant concentration of 0.08 M. The samples were kept at room temperature of 25 ± 1°C and were gently shaken once per day for three consecutive days and then left undisturbed for 2 weeks to reach equilibrium before assessing microemulsion phases.

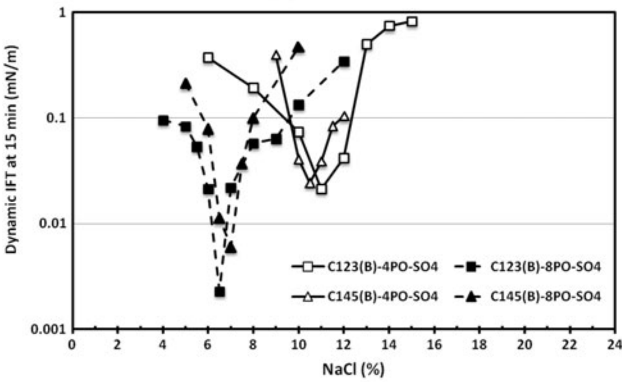
The dynamic interfacial tension (IFT) of oil and surfactant solution was determined using a spinning drop tensiometer (Model 500, University of Texas). The IFT measurements were made using 1–2 μL of oil injected into 300 μL of surfactant solution in a capillary tube. Reported IFT values were recorded at 15 min after oil injection.

Results and Discussions

Effect of PO Groups on Dynamic IFTs

Figure 3 presents the dynamic IFT values of four extended surfactants with tricaprylin and canola oil. It is noted that there are two pairs of extended surfactants having the same hydrocarbon chain but with different number of PO groups: C123(B)–4PO–SO_4Na vs. C123(B)–8PO–SO_4Na and C145(B)–4PO–SO_4Na vs. C145(B)–8PO–SO_4Na. This setup allows us to evaluate the effect of PO groups on IFT values. The results in Fig. 3 show that when the number of PO groups in the extended surfactants increases, both optimum salinity and minimum IFT values decrease. The decreased optimum salinities with increasing number of PO groups are expected because PO groups have been reported to be part of the hydrophobic tail of the surfactants [15]. What is of interest in this work is the relationship between number of PO groups and the ability to achieve ultralow IFT (<0.1 mN/m) with triglyceride oils. The results show that for the short-chain saturated triglyceride tricaprylin C8:0 (EACN = 16, [24]), all the studied extended surfactants (PO ≥ 4) were able to achieve ultralow IFT (≪0.1 mN/m). However, for canola oil (EACN = 18, [24]), the 4-PO extended surfactants could not achieve ultralow IFT (IFT* values were in the range of 0.2–0.5 mN/m). In contrast, the 8-PO extended surfactants were able to achieve IFT values much less than 0.1 mN/m for the canola oil. While we are not aware of triglyceride IFT data for 4-PO extended surfactants in the literature, the IFT values of the 8-PO extended surfactants in this work are in good agreement with IFT values reported for triolein and vegetable oils for the same types of extended surfactant [7, 8, 22–24] as summarized in Table 2.

(a) Tricaprylin



(b) Canola oil

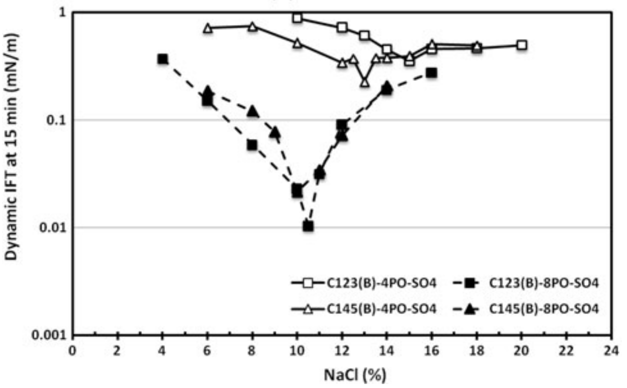


Fig. 3 Salinity scans of extended surfactants and tricaprylin and canola oil showing the effect of PO groups on S* and IFT*. Salinity scans were conducted at 0.1% wt. surfactant concentration at 25°C

Effect of Hydrocarbon Branching on IFTs

Figure 4 presents dynamic IFT values for a series of three extended surfactants with tricaprylin. Because the 4-PO extended surfactants could not achieve ultralow IFT with canola oil, the effect of hydrocarbon branching was studied only with tricaprylin. The three surfactants all have four PO groups but the structures of the hydrocarbon chains are

Table 2 Summary of published IFT values of triglyceride oils and extended surfactants

References	Extended surfactants	Triglyceride oils	% wt. NaCl	IFT (mN/m)
Witthayapanyanon et al. [22]	C_{14-15}–$(PO)_8$–SO_4Na (branched)	Peanut oil	10.5	0.061
		Canola oil	11.7	0.020
Do et al. [23]	C_{12}–$(PO)_{14}$–$(EO)_2$–SO_4Na (linear)	Peanut oil	7.5	0.012
		Canola oil	6.0	0.008
		Corn oil	7.5	0.006
Phan et al. [24]	C_{14-15}–$(PO)_8$–SO_4Na (branched)	Triolein (99% purity)	11.3	0.011
Do et al. [7]	C_{10}–$(PO)_{14}$–$(EO)_2$–SO_4Na (linear)	Peanut oil	6.0	0.012
		Canola oil	5.0	0.012
Phan et al. [8]	C_{14-15}–$(PO)_8$–SO_4Na (branched)	Canola oil	10.0	0.009

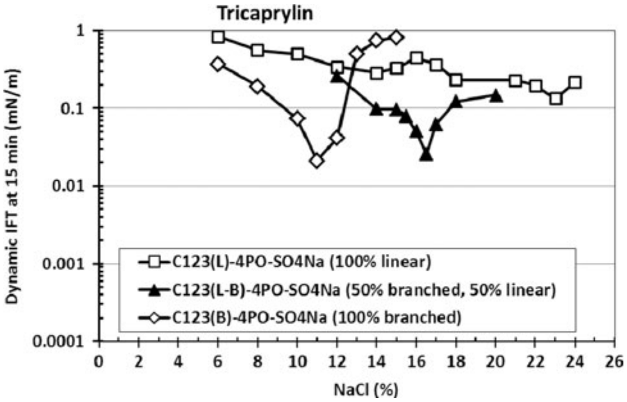


Fig. 4 Salinity scans of extended surfactants and tricaprylin showing the effect of surfactant hydrocarbon tail branching on S* and IFT*. Salinity scans were conducted at 0.1% wt. surfactant concentration at 25°C

different. The hydrocarbon chain of the C123(B)–4PO–SO_4Na surfactant is a mixture of branched alkyl of C12 and C13 (100% branched). The hydrocarbon chain of the C123(L)–4PO–SO_4Na surfactant is a mixture of linear alkyl of C12 and C13 (100% linear). The hydrocarbon chain of the C123(L–B)–4PO–SO_4Na surfactant is a mixture of branched alkyl of C12 and C13 and linear alkyl of C12 and C13 (50% branched, 50% linear). The results show that the optimum salinity decreased with increasing degree of branching in the hydrocarbon tail. For tricaprylin, the optimum salinity (S*) is 23% NaCl for C123(L)–4PO–SO_4Na while it is 11% NaCl for C123(B)–4PO–SO_4Na. The degree of surfactant branching also impacted the IFT values for tricaprylin, i.e. the branched surfactants (C123(B)–4PO–SO_4Na and C123(L–B)–4PO–SO_4Na) achieved ultralow IFT ($\ll$0.1 mN/m) while the linear surfactant C123(L)–4PO–SO_4Na had an IFT value of 0.13 mN/m.

Effect of Extended Surfactant Structure on Triglyceride Microemulsion Formation

Table 3 summarizes the results of triglyceride phase behavior studies of the selected extended surfactants with different hydrocarbon chain length, branching degree and number of PO groups. Optimum salinity and IFT values were obtained from dynamic IFT scans (i.e., oil injected into the IFT device rather than pre-equilibrated with oil in phase behavior studies). For the 4-PO extended surfactants, no microemulsion was observed with canola oil and only Winsor Type I and II microemulsions were observed with tricaprylin. At the salinities where Winsor Type III is expected, a sponge phase was observed, i.e. the surfactants separate out from the water phase and concentrate at the

Table 3 Microemulsion phase behavior of extended surfactants and triglyceride oils

Surfactant	Canola oil				Tricaprylin			
	S* (% NaCl)	IFT* (mN/m)	SP*[a] (mL/g)	Phase behavior	S* (% NaCl)	IFT* (mN/m)	SP*[a] (mL/g)	Phase behavior
C123(B)–4PO–SO_4	15.0	0.35	–	No microemulsion observed	11.0	0.021	–	Type I, II
C145(B)–4PO–SO_4	13.0	0.23	–	No microemulsion observed	10.5	0.024	–	Type I, II
C123(B)–8PO–SO_4	10.5	0.010	3.3	Type I, III, II	6.5	0.0023	5.5	Type I, III, II
C145(B)–8PO–SO_4	10.0	0.021	3.4	Type I, III, II	7.0	0.0060	6.0	Type I, III, II

[a] SP* = mL of oil (or water) in middle phase per g of surfactant; SP applies to Type III systems so is reported only when Type III systems were observed

oil/water interface but no oil was solubilized into this surfactant phase. The 8-PO extended surfactants were able to form Winsor Type I, III and II with both canola oil and tricaprylin. These observations were expected because these surfactants can achieve ultralow IFTs with both canola oil and tricaprylin. The solubilization parameters (SP*) for tricaprylin (5.5–6.0 mL/g) are significantly higher than those of canola oil (3.3–3.4 mL/g), but lower than values reported by Minana-Perez et al. (20 mL/g) [16] using extended surfactant systems without additives at 35°C. However, these values are comparable to values reported by Do et al. (6–10 mL/g for vegetable oils) [23] using extended surfactants and a combination of hydrophilic/lipophilic linkers.

General Discussion

The results in this work show that at least 8 propylene oxide groups are needed to achieve ultralow IFTs and to form middle phase microemulsion with canola oil, and that surfactant hydrocarbon branching facilitates ultralow IFTs as well as reduction in optimum salinity. Recent work by Prof. Salager's group [25, 26] suggested that the first 2-3 PO groups in the extended surfactant structure are most likely hydrated and assembled closed to the oil/water interface like depicted in Fig. 2. This would shorten the effective chain length of the extended surfactant. Using dynamic light scattering (DLS), Klaus et al. [27] also found that the radius of extended surfactant micelles is much smaller than the fully stretched length of the surfactant molecules which can be attributed to a disordered conformation of the PO groups. This might be the reason why at least 8 PO groups are needed to achieve ultralow IFTs and to form middle phase microemulsion with bulky triglyceride molecules like canola oil.

Only a limited number of works have evaluated the impact of branching on the performance of extended surfactants. Aoudia et al. [28] reported that the optimum salinity of twin-tailed extended surfactants is less sensitive in comparison to methyl branched extended surfactants with *n*-alkanes. In the same work cited above [27], Klaus et al. also found that on increasing the temperature, the curvature of extended surfactant micelles decreases leading to the formation of larger aggregates (bilayer or vesicles) which favor microemulsion formation and ultralow IFT. The authors conclude that this curvature reduction is due to a disordered conformation of the PO groups. We speculate that when increasing degree of branching in the hydrocarbon chain, micelle curvature was reduced in a similar way due to the disordered conformation of the branched alkyl groups. That might be the reason why IFT reduction was observed when degree of branching increased. However, future studies should systematically evaluate this trend.

Acknowledgments The authors would like to thank Geoff Russell and Victoria Stolarski, Sasol North America (Lake Charles, LA) for providing the extended surfactant samples. Funding for this work was provided by industrial sponsors of the Institute of Applied Surfactant Research at the University of Oklahoma: Akzo Nobel, Clorox, Conoco-Philips, Church and Dwight, Dow Chemical, Ecolab, Haliburton, Huntsman, Oxiteno, Procter & Gamble, Sasol North America, S.C. Johnson & Son, Shell Chemical; and by the Sun Oil Company Endowed Chair (David A. Sabatini).

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