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Formulation of Ultralow Interfacial Tension Systems Using Extended Surfactants

A. Witthayapanyanon^{a,d}, E.J. Acosta^b, J.H. Harwell^{a,d}, and D.A. Sabatini^{a,c,d,*}

^aUniversity of Oklahoma, Chemical, Biological, and Materials Engineering Department, Norman, Oklahoma, ^bUniversity of Toronto, Department of Chemical Engineering and Applied Chemistry, Toronto, Ontario, M5S 3E5 Canada,

^cUniversity of Oklahoma, Civil Engineering and Environmental Science Department, Norman, Oklahoma, and ^dInstitute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma

ABSTRACT: Inspired by the concept of lipophilic and hydrophilic linkers, extended surfactants have been proposed as highly desirable candidates for the formulation of microemulsions with high solubilization capacity and ultralow interfacial tension (IFT), especially for triglyceride oils. The defining characteristic of an extended surfactant is the presence of one or more intermediate-polarity groups between the hydrophilic head and the hydrophobic tail. Currently only limited information exists on extended surfactants; such knowledge is especially relevant for cleaning and separation applications where the cost of the surfactant and environmental regulations prohibit the use of concentrated surfactant solutions. In this work, we examine surfactant formulations for a wide range of oils using dilute solutions of the extended surfactant classes sodium alkyl polypropyleneoxide sulfate (R-(PO)_x-SO₄Na), and sodium alkyl polypropyleneoxide-polyethyleneoxide sulfate (R-(PO)_y-(EO)_z-SO₄Na). The IFT of these systems was measured as a function of electrolyte and surfactant concentration for polar and nonpolar oils. The results show that these extended surfactant systems have low critical micelle concentrations (CMC) and critical microemulsion concentrations (C_μC) compared with other surfactants. We also found that the unique structure of these extended surfactants allows them to achieve ultralow IFT with a wide range of oils, including highly hydrophobic oils (e.g., hexadecane), triolein, and vegetable oils, using only ppm levels of these extended surfactants. It was also found that the introduction of additional PO and EO groups in the extended surfactant yielded lower IFT and lower optimum salinity, both of which are desirable in most formulations. Based on the optimum formulation conditions, it was found that the triolein sample used in these experiments behaved as a very polar oil, and all other vegetable oils displayed very hydrophobic behavior. This unexpected triolein behavior is suspected to be due to uncharacterized impurities in the triolein sample, and will be further evaluated in future research.

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*To whom correspondence should be addressed at School of Civil Engineering and Environmental Science, Institute for Applied Surfactant Research, University of Oklahoma, 202 W. Boyd, Room 334, Norman, OK, USA, 73019-1024. E-mail: Sabatini@ou.edu

Abbreviations: ASC, average number of carbons in saturated chain; C_μC, critical microemulsion concentration; CMC, critical micelle concentration; DB, average number of double bonds of unsaturated chains; EACN, equivalent alkane carbon number; IFT, interfacial tension; SP, solubilization parameter; UC, fraction of unsaturated chains.

KEY WORDS: Dilute surfactant solution, extended surfactant, low interfacial tension, microemulsion, triglyceride, vegetable oils.

According to Winsor's premise (1), the oil and water solubilization capacity of microemulsion systems increases when the surfactant-oil and the surfactant-water interactions increase. Also, the optimum co-solubilization of oil and water is found when these two interactions are equal. An effective way of increasing these interactions is to enhance both the hydrophilicity of the head group and the hydrophobicity of the tail group of the surfactant while maintaining balanced affinity for the oil and water. However, surfactant solubility limits the magnitude to which this approach can be utilized; that is, as the hydrophobic tail gets longer, the surfactant eventually loses its water solubility (2). Graciaa *et al.* (3,4) first introduced the use of a lipophilic linker to effectively extend the length of the surfactant tail further into the oil phase without sacrificing water solubility of the surfactant; a long-chain alcohol is one example of such a linker molecule. Subsequently, the concept of the hydrophilic linkers was proposed as a way of compensating for the increased hydrophobicity of lipophilic linkers and to further improve the solubilization capacity of these systems (5,6,7). Hydrophilic linkers adsorb at the oil-water interface, thereby promoting surfactant-water interaction and loosening the surfactant packing at the interface (6). The combination of hydrophilic and lipophilic linkers has been shown to act as a pseudo surfactant, thereby reducing the amount of surfactant necessary for oil solubilization in middle phase microemulsions (8,9). However, not all linker molecules incorporate into the oil-water interface, rather some of these molecules partition either into the oil or water phases (8,9). To mitigate this undesirable separation, extended surfactants have been introduced (10,11,12,13,14).

Extended surfactants are surfactants in which groups of intermediate polarity, such as polypropyleneoxides or copolymers of propyleneoxides and ethyleneoxide, are inserted between the hydrocarbon tail and hydrophilic head group. Due to the resulting unique molecular structure, the surfactant is stretched out further into both the oil and

water phases, providing a smoother transition between the hydrophilic and hydrophobic regions of the interface, which provides a more suitable environment for solubilizing hydrophilic and lipophilic molecules. Additionally, the Gibbs adsorption equation leads us to expect that a thickening of the interfacial region between the two phases should result in an increase in adsorption at the interface and a reduction of interfacial tension.

Despite the relatively large molecular weight of these surfactants, they are water-soluble and can be formulated in relatively high electrolyte concentration while avoiding surfactant precipitation. Recently, several papers (11,14,15,16) have demonstrated the benefits of using these extended surfactants to enhance oil solubilization of microemulsion with highly hydrophobic oils, as well as triglyceride and vegetable oils.

Microemulsion formulation with triglycerides and conventional surfactants (surfactants other than extended surfactants) has proven to be a challenging task, likely due to the polar and at the same time hydrophobic nature of different regions in the triglyceride molecule. This is consistent with the extremely low solubilization parameters reported for these systems (17).

According to the Chun-Huh relationship, the oil/water solubilization capacity increases as the interfacial tension (IFT) of the microemulsion systems decreases, as shown in the following equation (18):

$$SP = \frac{C}{IFT^2} \quad [1]$$

where SP is known as the solubilization parameter (mL of oil/g of surfactant) of the microemulsion system, C is the Chun-Huh constant characteristic of the surfactant, and IFT is the IFT between excess oil and water phases (mN/m). Because large solubilization parameters have been reported for extended surfactant systems (11), the Chun Huh relationship predicts that these systems should produce ultralow IFT.

To date, the majority of extended-surfactant microemulsion systems have been Type IV single-phase microemulsions (14,15), due in large part to the occurrence of stable

macroemulsions in regions where Type III microemulsion systems were expected. These Type IV systems, which require elevated surfactant concentrations, are not particularly useful for most applications (detergency and soil, ground water, and wastewater remediation, etc.) where economics require that the surfactant be used at ppm levels in the formulation (15,16,19). In cleaning applications such as detergency and oil extraction, an additional requirement is to achieve low IFT within a reasonable contact time (minutes to tens of minutes).

Recently, it has been shown that an extended surfactant $C_{14-15}-(PO)_4-SO_4Na$ that could not form Type III middle phase microemulsions was still capable of producing ultralow IFT using only ppm-levels of the surfactant (15). These conditions were identified using electrolyte and surfactant concentration scans, and the dynamic and equilibrium IFT of these systems were measured. In the absence of middle phase microemulsions, which required higher surfactant concentrations, the optimum salinity was defined as the electrolyte concentration that produced the lowest IFT (15), and the critical microemulsion concentration ($C_{\mu C}$) was defined as the minimum surfactant concentration at which the ultralow IFT are attained (9,20).

In this work, the formulation of dilute extended surfactant formulations with a wide range of oils is studied, including petroleum hydrocarbons and vegetable oils. In the majority of studies, two extended surfactants were compared: $C_{14-15}-(PO)_8-SO_4Na$ and $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$. Although the molecular structure and molecular weight of these surfactants are quite different (see Figure 1), the HLB (hydrophilic lipophilic balance) values are only slightly different (see Table 1). The main difference between the two surfactants in Figure 1 is the additional PO and EO groups in $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$. To evaluate the effect of alkyl chain length, a third surfactant $C_{12-13}-(PO)_8-SO_4Na$ (see Table 1). A hydrophobic anionic surfactant, sodium dioctyl sulfosuccinate, was also formulated with Canola oil to compare the performance (IFT reduction) of these extended surfactants.

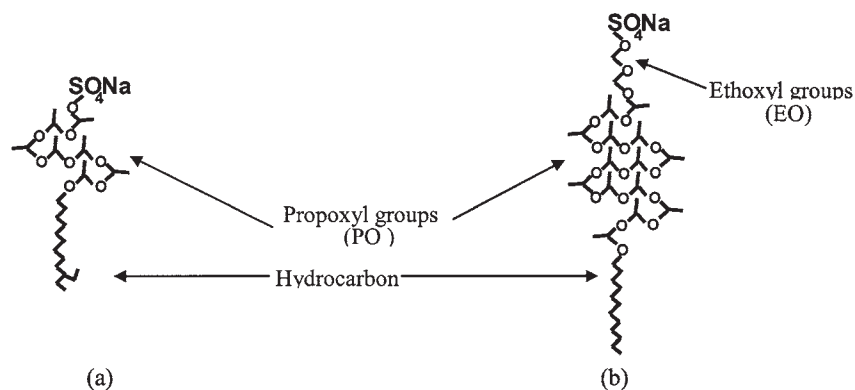


FIG. 1. Structure of extended surfactants: (a) alkyl-PO sulfate $C_{14-15}-(PO)_8-SO_4Na$, (b) alkyl-PO-EO sulfate $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$.

TABLE 1
Properties of the Extended Surfactants

Extended surfactant	Hydrocarbon chain length	No. of PO	No. of EO	% Active	HLB ^a	MW (g/mol)
Alkyl-PO _x -SO ₄ Na						
1. C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na	12–13	8	—	29.1	31.6	712.8
2. C _{14,15} H _{29,31} -(PO) ₈ -SO ₄ Na	14–15	8	—	29.6	30.6	715.5
Alkyl-PO _x -(EO) ₂ -SO ₄ Na						
1. C ₁₂ H ₂₅ -(PO) ₁₄ -(EO) ₂ -SO ₄ Na	12	14	2	24.1	31.8	1104

^aCalculated based on the Davies' group contribution factors: J.T. Davies. Proceedings 2nd Intern. Congress Surface Activity, vol. I, 426, Butterworth, London (1957).

The oils considered in this study are decane, hexadecane, triolein, canola oil, peanut oil, soya oil, corn oil, sunflower oil, and palm oil. The optimum electrolyte concentration (S^*) and the IFT at optimum formulation were studied for these systems. These results are analyzed using the surfactant affinity difference concept proposed by Salager *et al.* (21,22). Based on this approach, the relative hydrophobicity of the different oils is discussed, as well as the hydrophobicity of the extended surfactants. The values of IFT at optimum formulation and critical microemulsion concentration will be used to determine the efficacy and efficiency of these systems. Also, the relation between the properties of the surfactant formulations (optimum salinities, IFT, and critical microemulsion concentration) and the properties of each surfactant (HLB, CMC, surface area per molecule) are discussed. We thus demonstrate how the unique structure of extended surfactants allows us to achieve ultralow IFT at low surfactant concentrations with highly hydrophobic alkane oils and high molecular weight triglyceride and vegetable oils.

EXPERIMENTAL PROCEDURES

Materials. The extended surfactants evaluated in this work contain polyethylene and/or polypropylene oxide groups in between the hydrocarbon tail and sulfate head group. Two main classes of extended surfactant were used in this work. The first class of extended surfactant is a sodium alkyl polypropylene oxide sulfate (R-(PO)_x-SO₄Na) with the alkyl (R) group consisting of a branched hydrocarbon chain with 12 to 13 carbons (C₁₂₋₁₃) or 14 to 15 carbons (C₁₄₋₁₅) and with 8 propylene oxide units. The R-(PO)_x-SO₄Na surfactants were 29.4 wt% active with 0.1 wt% Na₂SO₄, 2.5 wt% of free oil, and 68 wt% water. These surfactants were donated by Sasol North American Inc (Lake Charles, LA).

The second class of extended surfactants evaluated is sodium linear-alkyl polypropoxylated polyethoxylated sulfate (R-(PO)_y-(EO)_z-SO₄Na) synthesized and donated by Huntsman Petrochemical Corp (Houston, TX) with 12 carbons in its hydrophobic tail (C₁₂), 14 propylene oxides and 2 ethylene oxide groups. This surfactant consists of 24.1 wt% active, 1–2 wt% Na₂SO₄, and 74–75 wt% water. The surfactant structures and properties are summarized in Table 1 and Figure 1. The extended surfactants were used as received from the manufacturers. Sodium dioctyl sulfosuccinate (Aerosol-OT,

anhydrous 99+%) was purchased from Fisher Scientific and used as received.

The following oils were purchased from Sigma-Aldrich (St. Louis, MO) at the concentration shown and used without further purification: glyceryl trioleate (triolein-65%, practical grade), canola oil (commercial canola cooking oil), peanut oil (Sigma), soya oil (Fluka), corn oil (Sigma), sunflower oil (Sigma), palm oil (commercial palm cooking oil), decane (99%+, anhydrous), hexadecane (99%+, anhydrous), and sodium chloride (99%+).

Methods. Dynamic IFT is the measurement of the time-dependent IFT using a spinning drop tensiometer (University of Texas, model 500). According to standard procedures (9,15,19), surfactant and sodium chloride concentrations were prepared in the aqueous solution and used as the dense phase. The IFT measurements were commenced immediately after injecting 1–3 μ L of the oil into a spinning drop tube containing the surfactant formulation. The IFT values were obtained as a function of time. Unless stated otherwise, IFT values are reported throughout this work for a ten minute reading. It was demonstrated that the dynamic IFT values reached equilibrium within 10 minutes. As a typical example, at the optimum salinity (0.13 M), the dynamic IFT values of C₁₂-(PO)₁₄-(EO)₂-SO₄Na at 10 min and 2 h are 0.0017 mN/m and 0.0019 mN/m, respectively. Additionally, 10 min dynamic IFT is a representative time for many cleaning applications (e.g., time scale of a washing cycle (19)).

Surface tension measurements on the surfactant solutions were performed with a Kruss K-10T tensiometer by Wilhelmy vertical plate technique at 30°C. Surfactant solutions were equilibrated for 2 h before data collection.

RESULTS AND DISCUSSION

Salinity scans of dilute solutions. Figure 2 illustrates the use of electrolyte scans with dilute surfactant solutions (10 mM). In particular, Figure 2 presents the values of dynamic IFT as a function of the electrolyte concentration for the systems triolein/C₁₄₋₁₅-(PO)₈-SO₄Na/brine, triolein/C₁₂-(PO)₁₄-(EO)₂-SO₄Na/brine, triolein/C₁₂₋₁₃-(PO)₈-SO₄Na/brine, and triolein/AOT/brine. The electrolyte concentration of 0.13 M is the optimum salinity (S^*) for the C₁₄₋₁₅-(PO)₈-SO₄Na system and 0.21 M is the optimum salinity (S^*) for the C₁₂₋₁₃-(PO)₈-SO₄Na system. In both cases the IFT reaches a minimum value

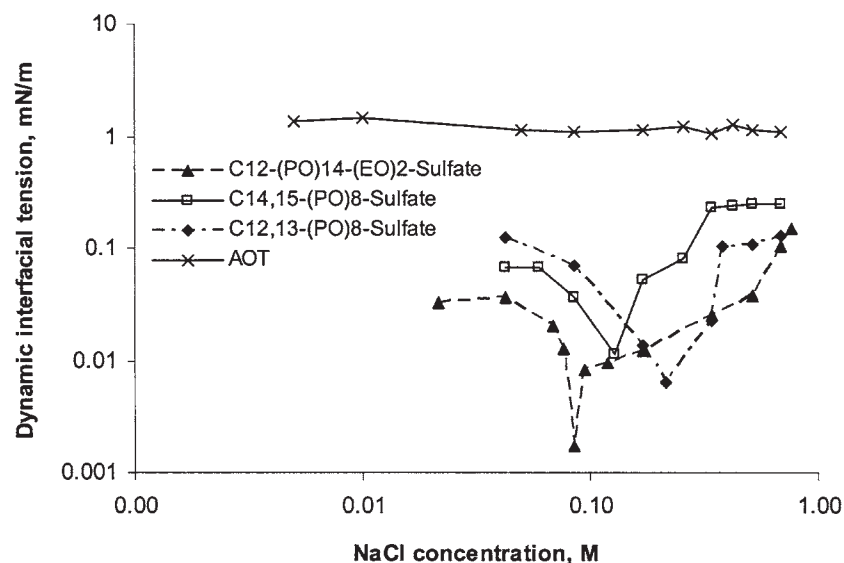


FIG. 2. Dynamic IFT as a function of electrolyte concentration (salinity scan) for the systems triolein- $C_{14-15}-(PO)_8-SO_4Na$ -brine (squares), triolein- $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ -brine (triangles), triolein- $C_{12-13}-(PO)_8-SO_4Na$ (diamonds), and triolein-AOT-brine (cross), surfactant concentration 10 mM. All readings taken after 10 min contact.

close to 0.01 mN/m. Similarly for the $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ system, a minimum IFT value close to 0.001 mN/m is observed at 0.09 M sodium chloride. For the conventional surfactant AOT the IFT remains above 1 mN/m for all values of electrolyte concentration.

To interpret these results, it is helpful to consider the different interactions in microemulsion systems. The Winsor R ratio helps explain the interrelation between the different interactions (1,2)

$$R = \frac{A_{SO_{NET}}}{A_{SW_{NET}}} = \frac{A_{SO} - A_{OO} - A_{LL}}{A_{SW} - A_{WW} - A_{HH}} \quad [2]$$

where $A_{SO_{NET}}$ is the net interaction between the surfactant and oil, $A_{SW_{NET}}$ is the net interaction between the surfactant and water, A_{SO} is the interaction between the surfactant and oil, A_{SW} is the interaction between the surfactant and water, A_{OO} is the interaction energy among oil molecules, A_{LL} is the interaction among the tails of the surfactant molecules, A_{WW} is the interaction energy among the water molecules, and A_{HH} is the interaction among the surfactant heads.

As mentioned in the introduction section, the optimum formulation is obtained when the net interactions $A_{SW_{NET}}$ and $A_{SO_{NET}}$ are equal (this results in $R = 1$). Also, the solubilization increases and the IFT decreases when each of these interactions is larger but equal. The addition of electrolyte in each of these formulations is used to suppress the double layer around the anionic group of the surfactant, thus reducing A_{SW} , and $A_{SW_{NET}}$. A larger optimum electrolyte concentration suggests that the surfactant-oil interaction (A_{SO}) is small because more electrolyte is required to reduce A_{SW} to the A_{SO} value.

In the particular case of Figure 2, $C_{12}-(PO)_{14}-(EO)_2-$

SO_4Na shows the lowest optimum salinity (and the thus largest A_{SO}). Because A_{SO} is largest (and thus the balanced A_{SW} is also largest) the co-solubilization of oil and water is expected to be largest, and according to equation 1 the IFT is expected to be the lowest. In fact, the IFT at optimum formulation for this surfactant is close to one order of magnitude lower than the optimum values observed for the PO extended surfactants (0.0017 mN/m vs. 0.0113 mN/m). The results suggest that additional PO and EO groups (14PO, 2EO vs. 8PO) increase the interaction with triglyceride molecules, likely because these groups match the polarity of the glycerol ester groups of the triglyceride (triolein in this case). This hypothesis would also explain why conventional surfactants (such as AOT in Figure 2) are not capable of producing microemulsions or solutions with ultralow IFT for triglyceride oils.

When comparing the optimum electrolyte concentration for $C_{14-15}-(PO)_8-SO_4Na$ and $C_{12-13}-(PO)_8-SO_4Na$ (0.13 M vs. 0.21 M, respectively), it is clear that when the tail length of the surfactant is smaller, the optimum salinity increases, suggesting that the interaction A_{SO} is smaller. The optimum IFT for both systems is comparable, which suggests that the changes of the net interactions are minor, and that factors such as A_{LL} , and A_{HH} should be considered.

One important point of consideration is that, according to Table 1, the surfactant $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ has a slightly higher HLB value than $C_{14-15}-(PO)_8-SO_4Na$ which would imply that this is a more hydrophilic surfactant. Yet, as discussed above, the lower optimum salinity for this surfactant (Fig. 2) indicates that this surfactant is more hydrophobic (larger A_{SO}) than its alkyl-PO-sulfate counterpart. This shows that the HLB parameter alone does not completely capture the nature of the interactions between extended sur-

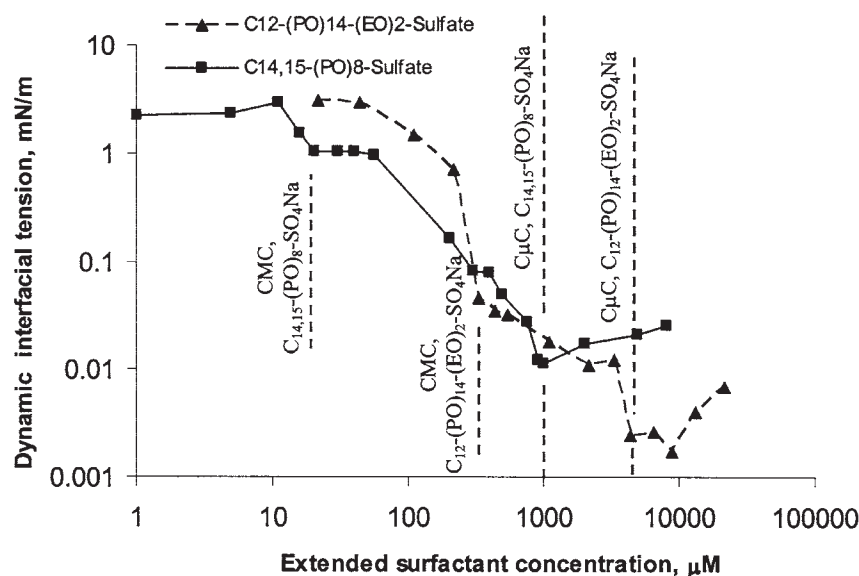


FIG. 3. Dynamic surface tension versus surfactant concentration at optimum electrolyte concentration for the systems triolein- $C_{14,15}-(PO)_8-SO_4Na$ -0.2 M NaCl brine (squares) and triolein- $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ -0.015 M brine (triangles). All readings after 10 min contact.

factant and triglycerides, probably due to the slightly polar environment induced by the presence of the PO groups in the surfactant.

Surfactant concentration scans. In this set of experiments, the electrolyte concentration was fixed at the optimum salinity, and the dynamic IFT was measured against triolein as a function of surfactant concentration for 0.2 M NaCl concentration. Figure 3 shows the dynamic IFT for the systems triolein/ $C_{14,15}-(PO)_8-SO_4Na$ /brine, and triolein/ $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ /brine. The trend of decreasing IFT with the increase in surfactant concentration follows the trend previously observed in systems where equilibrium IFT values were measured (9,15). This decrease in IFT follows two steps. The first step corresponds to the absorption of the surfactant at the oil-water interface, which occurs at concentrations less than the CMC. The second step corresponds to the change in curvature of the micelles which ends at the point where the first droplet of microemulsion forms (the $C_{\mu}C$) (9). Although an intermediate plateau typically separates the two steps, this is not completely obvious in the curves of Figure 3, potentially due to the dynamic nature of the experiment.

It should be noted that, at least to our knowledge, this is the first time that ultralow IFT with triglycerides has been reported using surfactant concentrations in the range of 0.1 to 1.0 mM without the addition of co-oils and/or alcohol. This finding is of great significance for applications such as detergency and other cleaning processes where oil removal performance correlates with lower IFT (19).

The $C_{\mu}C$ value for $C_{14,15}-(PO)_8-SO_4Na$ is close to five times smaller than the $C_{\mu}C$ of $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ (1,000 μM vs. 4,365 μM , respectively). Although this suggests that $C_{14,15}-(PO)_8-SO_4Na$ is a more efficient surfactant, a

closer look at the data shows that the IFT for $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$ is lower. As will be discussed later, the $C_{\mu}C$ obtained for these microemulsion systems correlates with the CMC of the pure surfactants.

One final observation related to Figure 3 is that there is a slight increase in the IFT above the $C_{\mu}C$. This is observed for both surfactants, and it seems to be correlated with the fact that gel phases were obtained instead of the middle phase microemulsions, which is consistent with previous observations (14). The physical explanation for this phenomenon is still unknown.

Formulation of ultralow IFT systems with a range of oils. In the next set of experiments, salinity scans were conducted using the surfactants described above along with hydrophobic oils (decane, hexadecane) and a range of vegetable oils. Table 2 summarizes the optimum salinity and minimum IFT obtained with these oils and the surfactant $C_{14,15}-(PO)_8-SO_4Na$. Table 3

TABLE 2
Summary of the Optimum Salinity (S^*) and the Optimum Dynamic IFT (IFT*) with Various Kinds of Oils^a

Oil	S^* (M)	IFT* (mN/m)	EACN
AOT			
Canola oil	1.60	1.2400	
$C_{14,15}H_{29,31}-(PO)_8-SO_4Na$			
Decane	1.00	0.0168	10
Hexadecane	1.40	0.0046	16
Triolein	0.2	0.011	-18 ^b
Peanut oil	1.8	0.061	20 ^b
Canola oil	2.0	0.020	22 ^b

^aThe IFT was measured after 10 min of contact using a spinning drop tensiometer at 0.2 wt% $C_{14,15}-(PO)_8-SO_4Na$.

^bCalculated using Equation 5.

TABLE 3
Summary of the Optimum Salinity (S^*) and the Optimum Dynamic IFT (IFT*) with Various Kinds of Oils^a

Oil	S^* (M)	IFT* (mN/m)	EACN
Decane	0.088	0.021	10
Hexadecane	0.13	0.003	16
Triolein	0.015	0.0017	-16 ^b
Soy oil	0.15	0.0048	18 ^b
Corn oil	0.13	0.0015	16 ^b
Canola oil	0.16	0.0013	18 ^b
Sunflower oil	0.12	0.0052	14 ^b
Peanut oil	0.15	0.0015	18 ^b
Palm oil	0.12	0.0057	14 ^b

^aThe IFT was measured after 10 min of contact using a spinning drop tensiometer at 0.2 wt% $C_{14-15}-(PO)_8-SO_4Na$.

^bCalculated using Equation 6

summarizes the same set of data obtained with the surfactant $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$. The optimum salinity presented in these tables gives an indication of how hydrophobic an oil phase is. This hydrophobicity can be expressed in terms of the equivalent alkane carbon number (EACN) as defined by Salager *et al.* (21):

$$\ln(S^*) = K(EACN) + f(A) - \sigma + aT\Delta T \quad [3]$$

where S^* is the optimum salinity of microemulsion system, EACN is equivalent alkane carbon number of oil, $f(A)$ is a function of surfactant and cosurfactant concentration, σ is a function of alcohol type and concentration, and T is the temperature. From Equation 3, the optimum salinity is a function of the EACN of the oil. For hydrocarbons such as decane and hexadecane the EACN value corresponds to the alkyl chain length, 10 and 16, respectively.

Considering that for each surfactant the term $f(A) - \sigma + aT\Delta T$ is a constant, which we will call b , Equation 3 thus takes a linear form with respect to the logarithm of optimum salinity:

$$\ln(S^*) = K(EACN) + b \quad [4]$$

This simplified formulation equation can be calibrated with two known values of optimum salinity and EACN. Using the optimum salinity values for decane and hexadecane (EACN values of 10 and 16, respectively) the resulting equations are as follows:

$$\begin{aligned} \text{For } C_{14-15}-(PO)_8-SO_4Na \\ \ln(S^*) = 0.053 \times EACN - 0.52 \end{aligned} \quad [5]$$

$$\begin{aligned} \text{For } C_{12}-(PO)_{14}-(EO)_2-SO_4Na \\ \ln(S^*) = 0.069 \times EACN - 3.1 \end{aligned} \quad [6]$$

One important observation from these equations is that the K values (0.053 and 0.069) are relatively small compared with the typical value of 0.17 for conventional anionic surfactants (1,2). In other words, this means that, in microemulsion or ultralow IFT systems, extended surfactants are not as electrolyte-sensitive as conventional anionic sur-

TABLE 4
Selected Composition Parameters of Vegetable Oils and Calculated EACN (23)

Oil	Avg. length of saturated chain (ASC)	% Unsaturated chains (UC)	Avg. number of double bonds (DB)	EACN calculated ^a
Triolein	N.A.	100	1	-17
Soy oil	16.5	85	1.7	16
Corn oil	16.3	87	1.7	16
Canola oil	16.6	94	1.4	17
Sunflower oil	16.8	88	1.8	17
Peanut oil	19.5	82	1.4	22
Palm oil	16.1	50	1.2	13

^aCalculated using Equation 8.

factants, probably due to the nonionic nature of the PO and EO groups that are next to the ionic head group. The EO and PO chains potentially arrange in the extended surfactants in such a way to allow the surfactant membrane to minimize the repulsion between the sulfate groups, which reduces their dependence on electrolyte in forming a low energy surfactant membrane. Interestingly, the relatively invariable dynamic IFT value of the conventional surfactant AOT in Figure 2 seems to contradict the above explanation. In fact, the limited response of AOT to salinity reflects that AOT is an ineffective choice for these oils and does not form microemulsions or ultralow IFT with these oils studied here.

Using Equations 5 and 6, and the optimum salinity obtained through the electrolyte scans, the EACN values for each of the vegetable oils were calculated, as summarized in Tables 2 and 3. The most remarkable fact that comes out of these EACN values is that triolein has a highly negative EACN value whereas the vegetable oils have positive values. Although the EACN values for triolein, canola, and peanut oil were not exactly the same between the two surfactant systems, they were close enough to validate the relative magnitude of these values.

To explore the variation in EACN for triolein and the vegetable oils, three molecular structure parameters were considered: the average number of carbons in the saturated chains (ASC), the fraction of the unsaturated chains (UC), and the average number of double bonds of the unsaturated chains (DB). These values were calculated from typical composition data (23), and are summarized in Table 4. To correlate these composition parameters to the calculated EACN values for these triglyceride molecules, the following linear regression was investigated (23):

$$EACN_{\text{triglyceride}} = c_1 \times ASC + c_2 \times UC + c_3 \times DB + c_4 \quad [7]$$

A sensitivity analysis revealed that DB had little impact on the EACN (an increment of 1 additional double bond changed the EACN value by less than 1%). The following simplified correlation was found (23):

$$EACN_{\text{triglyceride}} = 2.05 \times ASC + 0.071 \times UC - 24 \quad [8]$$

TABLE 5
Critical Micelle Concentration (CMC) and Area Per Molecule (A_{\min}) of Conventional and Extended Surfactants

Surfactant	No salt		0.2 M NaCl	
	CMC (μM)	A_{\min} (\AA^2)	CMC (μM)	A_{\min} (\AA^2)
$\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ (Varadaraj, 1992)	7,900	52.5	—	—
Branch $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ (Varadaraj, 1992)	14,200	95	—	—
$\text{C}_{14}\text{H}_{29}\text{SO}_4\text{Na}$ (Lange, 1968)	2,100 ^a	56 ^b	—	—
$\text{C}_{12-13}\text{H}_{25-37}-(\text{PO}_8)-\text{SO}_4\text{Na}$	130	153	14	68
$\text{C}_{14-15}\text{H}_{29-31}-(\text{PO}_8)-\text{SO}_4\text{Na}$	33	133	5	116
$\text{C}_{12}\text{H}_{25}-(\text{PO}_{14})-(\text{EO}_2)-\text{SO}_4\text{Na}$	80	200	8	147

^aLange, 1968

^bHuber, 1991, Rosen, 1996

The R^2 correlation factor between the values calculated with Equation 8 and the values calculated using Equations 5 and 6 is 0.97. More importantly, Equation 8 reveals that there is a constant negative factor for triglycerides ($c_4 = -24$), which could correspond to the polarity of the glycerol group. The positive value of c_1 indicates that the saturated hydrocarbon chains are the largest contributing factor to the hydrophobicity of triglycerides. On the other hand, unsaturated chains do contribute to the hydrophobicity of the triglyceride but not as much as their saturated counterparts.

One last observation regarding the formulation of ultralow IFT systems with vegetable oils is that the IFT achieved with $\text{C}_{12}-(\text{PO})_{14}-(\text{EO})_2-\text{SO}_4\text{Na}$ were close to one order of magnitude smaller than those obtained with $\text{C}_{14-15}-(\text{PO})_8-\text{SO}_4\text{Na}$ (see Fig. 3 and Tables 2 and 3). Nonetheless the IFT with decane and hexadecane were almost the same for both surfactants. This suggests that the interaction between extended surfactants and alkanes are driven by the alkyl groups while the interaction with triglycerides are driven by the PO and EO groups.

The EACN values for triolein in Tables 2, 3, and 4 should be qualified. As described in the Materials section, the triolein used in these measurements was a 65%, practical grade. The most likely explanation for the anomalous EACN values obtained for triolein in these experiments is that the sample contained significant levels of fatty acids and monoglycerides, which made it behave as though it were a much more polar oil. Although beyond the scope of this research, this phenomenon will be further explored in future work.

Correlation between extended surfactant properties and performance. Because of the limited availability of extended surfactants, we are not able to systematically compare the effect of varying the number of EO and PO groups for a constant alkyl chain length and PO groups of extended surfactants. However, Minana-Perez *et al.* (11) reported that the presence of EO groups in extended surfactant structures was reported to give outstanding solubilization parameters (10–30 mL/g surfactant) and three-phase behavior with triglycerides such as soya oils. They also mentioned that extended surfactants consisting of both EO and PO groups in surfactant structure have a dual anionic and nonionic character, which was reflected

in the lower K value obtained for these surfactants (Equations 5 and 6).

Because of the exciting potential of extended surfactants to lower the IFT of triglyceride, vegetable oils, highly hydrophobic oils such as hexadecane, it is valuable to characterize the interfacial properties of these extended surfactants, such as the critical micelle concentration (CMC) and the surface area per molecule of the surfactant (A_{\min}). A_{\min} and CMC values were measured from surface tension data without added salt and with 0.2 M NaCl, and at 30°C, as presented in Table 5. CMC values were determined as the intersection of two linear portions of surface tension (γ) vs. log concentration (log C) diagram. The area per molecule (A_{\min} , $\text{\AA}^2/\text{molecule}$) is also determined from this same plot (24). Figure 4 shows the γ vs. log C for the three extended surfactants, $\text{C}_{14-15}-(\text{PO})_8-\text{SO}_4\text{Na}$, $\text{C}_{12-13}-(\text{PO})_8-\text{SO}_4\text{Na}$ and $\text{C}_{12}-(\text{PO})_{14}-(\text{EO})_2-\text{SO}_4\text{Na}$.

According to Table 5, it is seen that all of the extended surfactants have CMC values much lower than conventional C_{12} and C_{14} surfactants (24,25). Furthermore, we observe a decrease in CMC of the extended surfactants as the alkyl chain length increases (130 μM for $\text{C}_{12-13}-(\text{PO})_8-\text{SO}_4\text{Na}$ and 33 μM for $\text{C}_{14-15}-(\text{PO})_8-\text{SO}_4\text{Na}$); this four-fold decrease is similar in ratio to the decrease in conventional C_{12} to C_{14} surfactants in Table 5 (7,900 to 2,100 μM , respectively). We thus observe that the introduction of EO and/or PO groups has a significant effect on the CMC. Moreover, the lower CMC of $\text{C}_{14-15}-(\text{PO})_8-\text{SO}_4\text{Na}$ is consistent with the lower CMC observed for this surfactant. This is consistent with previous observations that the two phase transitions (monomer-micelle, and micelle-microemulsion) are correlated (9).

The data of Table 5 indicate that the extended surfactants have a large A_{\min} as compared with conventional surfactants. Moreover, the presence of two EO groups in $\text{C}_{12}-(\text{PO})_{14}-(\text{EO})_2-\text{SO}_4\text{Na}$ further increases A_{\min} . Dahanayake *et al.* (26) reported that the introduction of the second EO group does increase the A_{\min} . This increase in surface area may create additional interfacial area were the polar glycerol groups can penetrate the palisade layer. In addition this larger surface area may help explain the shielding effect (lower K values) provided by the PO and EO groups. Thus, adding PO and EO groups can increase the area per molecule, but still achieves ultralow CMC values and ultralow IFT values, suggesting that the increased hydrophobic interaction resulting from the extended tail helps offset the lower packing density.

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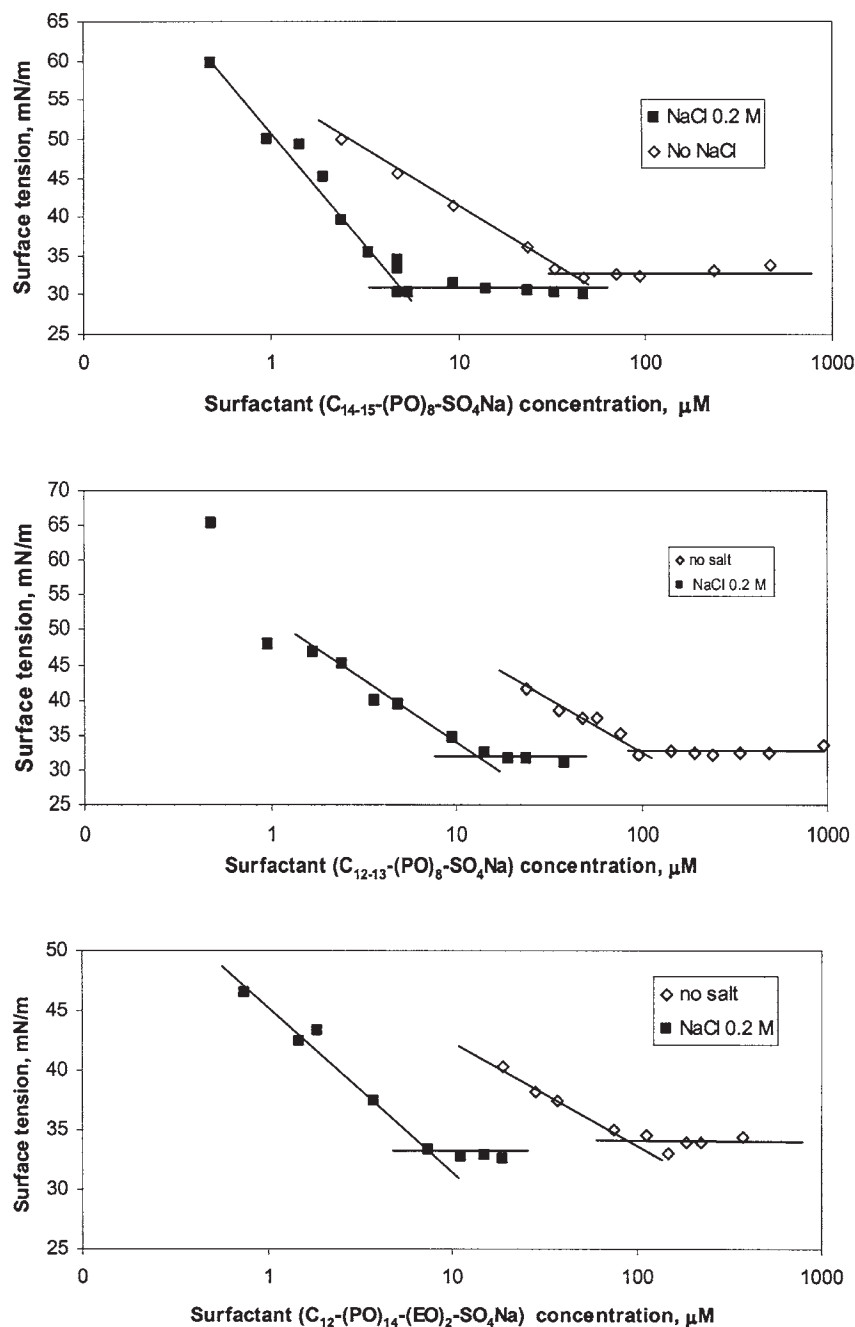


FIG. 4. Surface tension of extended surfactants with and without salt: (a) $C_{14-15}-(PO)_8-SO_4Na$, (b) $C_{12-13}-(PO)_8-SO_4Na$, and (c) $C_{12}-(PO)_{14}-(EO)_2-SO_4Na$.

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REFERENCES

1. Bourrel, M., and R. Schecter, *Microemulsions and Related Systems*, Marcel Dekker, New York, 1988.
2. Salager, J.L., R.E. Antón, D.A. Sabatini, J.H. Harwell, E.J. Acosta, and L.I. Tolosa, Enhancing Solubilization in Microemulsions—State of the Art and Current Trends, *J. Surfact. Deterg.* 8:3–21 (2005).
3. Graciaa, A., J. Lachaise, C. Cucuphat, M. Bourrel, and J.L. Salager, Improving Solubilization in Microemulsions with Additives. 1. The Lipophilic Linker Role, *Langmuir* 9:669–672 (1993).
4. Graciaa, A., J. Lachaise, C. Cucuphat, M. Bourrel, and J.L. Salager, Improving Solubilization in Microemulsions with Additives. 2. Long Chain Alcohols as Lipophilic Linkers, *Langmuir* 9:3371–3374.
5. Uchiyama, H., E. Acosta, S. Tran, D.A. Sabatini, and J.H. Har-

- well, Supersolubilization in Chlorinated Hydrocarbon Microemulsions: Solubilization Enhancement by Lipophilic and Hydrophilic Linkers, *Ind. Eng. Chem. Res.* 39:2704–2708 (2000).
6. Acosta, E., H. Uchiyama, D.A. Sabatini, and J.H. Harwell, The Role of Hydrophilic Linkers, *J. Surfact. Deterg.* 5:151–157 (2002).
 7. Sabatini, D.A., E.J. Acosta, and J.H. Harwell, Linker Molecules in Surfactant Mixtures, *J. Colloid Interface Sci.* 8:316–326 (2003).
 8. Acosta, E., S. Tran, H. Uchiyama, D.A. Sabatini, and J.H. Harwell, Formulating Chlorinated Hydrocarbon Microemulsions Using Linker Molecules, *Environ. Sci. Technol.* 36:4618–4624 (2002).
 9. Acosta, E. J., J.H. Harwell, and D.A. Sabatini, Self-assembly in Linker-Modified Microemulsions, *J. Colloid Interface Sci.* 274:652–664 (2004).
 10. Miñana-Pérez, M., A. Graciaa, J. Lachaise, and J.L. Salager, Solubilization of Polar Oils in Microemulsion Systems, *Prog. Colloid Polym. Sci.* 98:177–179 (1995).
 11. Miñana-Pérez, M., R.E. Antón, A. Graciaa, J. Lachaise, and J.L. Salager, Solubilization of Polar Oils with Extended Surfactants, *Colloid Surfaces A* 100:217–224 (1995).
 12. Scorzza, C., P. Godé, P. Martin, M. Miñana-Pérez, J.L. Salager, and P. Villa, Synthesis and Surfactant Properties of a New “Extended” Glucidoamphiphile Made from d-Glucose, *J. Surfact. Deterg.* 5:331 (2002).
 13. Scorzza, C., P. Godé, G. Goethals, P. Martin, M. Miñana-Pérez, J.L. Salager, A. Usabillaga, and P. Villa, Another New Family of “Extended” Glucidoamphiphiles. Synthesis and Surfactant Properties for Different Sugar Head Groups and Spacer Arm Lengths, *J. Surfact. Deterg.* 5:337 (2002).
 14. Huang, L., A. Lips, and C. Co, Microemulsification of Triglyceride Sebum and the Role of Interfacial Structure on Bicontinuous Phase Behavior, *Langmuir* 20:3559–3563 (2004).
 15. Childs, J., E. Acosta, J.F. Scamehorn, and D.A. Sabatini, Surfactant-Enhanced Treatment of Oil-Based Drill Cuttings, *J. Energy Res. Technol.* 127:153–162 (2005).
 16. Yanatatsaneejit, U., P. Rangsunvigit, J.F. Scamehorn, and S. Chavadej, Diesel Removal by Froth Flotation Under Low Interfacial Tension Conditions I: Foam Characteristics, Coalescence Time, and Equilibration Time, *Sep. Sci. Tech.* 40:1537 (2005).
 17. Christov, N.C., N.D. Denkov, P.A. Kralchevsky, G. Broze, and A. Mehreteab, Kinetics of Triglyceride Solubilization by Micellar Solutions of Nonionic Surfactant and Triblock Copolymer1. Empty and Swollen Micelles, *Langmuir* 18:7880–7886 (2002).
 18. Huh, C. Interfacial Tensions and Solubilizing Ability of a Microemulsion Phase That Coexists with Oil and Brine, *J. Colloid Interface Sci.* 71:408–426 (1979).
 19. Tongcumpou, C., E.J. Acosta, L.B. Quencer, A.F. Joseph, J.F. Scamehorn, D.A. Sabatini, S. Chavadej, and N. Yanumet, Microemulsion Formation and Detergency with Oily Soils: II. Detergency Formulation and Performance, *J. Surfact. Deterg.* 6:205–214 (2003).
 20. Aveyard, R., B.P. Binks, and P.D.I. Fletcher, Interfacial Tensions and Aggregate Structure in Pentaethylene Glycol Monododecyl Ether/Oil/Water Microemulsion Systems, *Langmuir* 5:1210 (1989).
 21. Salager, J.L., J. Morgan, R.S. Schechter, W.H. Wade, and E. Vasquez, Optimum Formulation of Surfactant-Oil-Water Systems for Minimum Tension and Phase Behavior, *Soc. Petrol. Eng. J.* 19:107–115 (1979).
 22. Salager, J.L., N. Márquez, A. Graciaa, and J. Lachaise, Partitioning of Ethoxylated Octylphenol Surfactants in Microemulsion-Oil-Water Systems: Influence of Temperature and Relation Between Partitioning Coefficient and Physicochemical Formulation, *Langmuir* 16:5534–5539 (2000).
 23. Campbell, E., Baker, N., and Bandurraga, M. eds., *Food Fats and Oils*, Institute of Shortening and Edible Oils, Washington, DC, 1999, p. 27.
 24. Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd ed., John Wiley and Sons, New York, 1989.
 25. Lange, H., and M.J. Schwuger, Micelle Formation and Kraft-Points in a Homologous Series of Sodium-N-Alkyl Sulfates Including Odd-Numbered Members, *Kolloid Z.Z. Polym.* 223:145 (1968).
 26. Dahanayake, M., A.W. Cohen, and M.J. Rosen, Relationship of Structure to Properties of Surfactants: 13 Surface and Thermodynamic Properties of Some Oxyethylenated Sulfates and Sulfonates, *J. Phys. Chem.* 90:2413–2418 (1986).

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Anuradee Witthayapanyanon received her BS (2001) in Chemical Engineering from the King Mongkut University of Technology Thon Buri, Thailand. In 2003, she obtained her MS in Petrochemical Technology from Chulalongkorn University, Thailand. She is currently a Ph.D candidate in Chemical Engineering at the University of Oklahoma.

Edgar J. Acosta received his BS from Universidad de Zulia, Venezuela (1996), and his MS and PhD in Chemical Engineering from the University of Oklahoma (2004). He is an Assistant Professor of Chemical Engineering and Applied Chemistry at the University of Toronto in Ontario, Canada. His research interests include microemulsion formulation and modeling and the study of surfactant synergism as applied to environmental, consumer product, industrial and human health sectors.

Jeffrey H. Harwell is a Conoco/DuPont Professor of Chemical, Biological, and Materials Engineering at the University of Oklahoma. He received his BA (1974) and MS (1979) from Texas A&M University and his PhD (1983) from the University of Texas. His research focuses on fundamental and applied characteristics of surfactants in industrial and environmental applications.

David A. Sabatini, David Ross Boyd Professor and Sun Oil Company Chair of Civil Engineering and Environmental Science, is Associate Director of the Institute of Applied Surfactant Research at the University of Oklahoma. He received his BS from the University of Illinois (1981), his MS from Memphis State University (1985) and his PhD from Iowa State University (1989). His research focuses on surfactant-based subsurface remediation, surfactant-based alternatives to organic solvents, and advanced microemulsions for cleaning systems.