

Relationship of Structure to Properties of Surfactants. 15 Isomeric Sulfated Polyoxyethylenated Guerbet Alcohols¹

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The properties at 25°C in aqueous 0.1M NaCl at the aqueous solution/air, aqueous solution/hexadecane, and aqueous solution/hydrophobic solid interfaces of two isomeric Guerbet alcohol-derived surfactants $C_8H_{17}CH(C_6H_{13})CH_2(OC_2H_4)_5SO_4Na$, one in which the octyl and hexyl groups are both linear (L isomer), the other in which they are both highly branched (B isomer), have been investigated and compared in some cases with commercial sodium linear dodecylbenzenesulfonate (LAS). The cmc value increases, the pC_{20} value decreases, and the ΔG_{ad}° value becomes less negative in the order: L isomer - B isomer - LAS. The minimum area/molecule at the aqueous solution/air interface increases in the order: LAS \ll L isomer $<$ B isomer.

The L isomer is slightly more hydrophobic than the B isomer, and both are considerably more surface-active than LAS. The greater steric inhibition to micellization in the B isomer results in the lowest minimum surface tension. Both isomers have similar minimum interfacial tension values against hexadecane. Unusually small minimum area/molecule values for the two isomers at the aqueous solution/hydrophobic solid interface may indicate multilayer adsorption there. Both isomers are more efficient at reducing the contact angle than LAS. Mixtures of the B isomer with the corresponding unsulfated Guerbet alcohol show only weak interaction between the two. No synergism in surface (or interfacial) tension reduction efficiency or micelle formation exists at either the aqueous solution/air or aqueous solution interface but the mixture does show synergism in surface (or interfacial) tension reduction effectiveness, yielding a surface tension value of 28.2 dynes/cm, and an interfacial tension value of 0.1 dyne/cm against hexadecane. Draves wetting times increase in the order: B isomer $<$ LAS $<$ L isomer, and Ross-Miles initial foam heights decrease in the order B isomer \approx LAS $>$ L isomer.

Surfactants based on Guerbet alcohols, $RCH(R^1)CH_2OH$, where R^1 has two carbon atoms less than R , are of both scientific and practical interest. Scientifically, they represent a class of surfactants where the hydrophobic group is branched at a fixed position, thus permitting the effect of this branching on physicochemical properties to be determined unambiguously. Practically, the Guerbet alcohols can readily be obtained from both natural and synthetic alcohols (1). Because of this interest, an investigation into the surface and interfacial properties of these surfactants at various interfaces was undertaken.

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The results reported here are for the sodium salts of two isomeric sulfated polyoxyethylenated C_{16} Guerbet alcohols, one in which R and R^1 are both linear, the other in which they are both highly branched. In addition, some of their surface and interfacial properties are compared with those of a commercial sodium linear dodecylbenzenesulfonate (LAS).

EXPERIMENTAL

Materials. $C_8H_{17}CH(C_6H_{13})CH_2(OC_2H_4)_5SO_4Na$ with linear octyl and hexyl groups ($C_{16}LGEO_5S$) and a homogeneous polyoxyethylene chain was obtained from Exxon Research and Engineering Corp., Annandale, NJ. Two-phase titration with Hyamine 1622, using mixed indicator (2) showed a purity of 95.0%. Elemental analysis: found C=55.30, H=9.83, S=5.24, Na=4.38; calculated C=55.29, H=9.46, S=5.68, Na=4.07. The isomeric compound with highly branched octyl and hexyl groups ($C_{16}BGEO_5S$) and a homogeneous polyoxyethylene chain was also obtained from Exxon Research and Engineering Corp. Two phase titration showed a purity of 91.3%. Elemental analysis: found C=54.98, H=9.84, S=5.75, Na=4.39; calculated C=55.29, H=9.46, S=5.68, Na=4.07. The commercial sodium linear dodecylbenzenesulfonate (LAS) was C-550 LAS (Vista Chemical Co., Ponca City, OK).

Before being used for surface tension, interfacial tension, or contact angle measurements, aqueous solutions of the surfactants (in water that had been first deionized and then distilled twice, the last time from alkaline permanganate solution through a three ft-high Vigreux column with quartz condenser and receiver) were further purified by repeated passage (3) through minicolumns of octadecylsilanized silica gel to remove any traces of impurities more surface-active than the parent compound. The concentration of surfactant in the effluent from these columns was determined by two-phase mixed indicator titration with Hyamine 1622.

Sodium chloride used to increase the ionic strength of solutions was analytical grade material, which was then baked for several hours in a porcelain casserole at red heat to remove traces of organic compounds.

Surface tension measurements. Measurements were made by the Wilhelmy plate technique, with a sandblasted platinum plate of a ca. 5-cm perimeter. Instruments were calibrated against quartz-condensed water (specific conductivity $1.1 \times 10^{-6} \Omega^{-1}cm^{-1}$ at 25°C) each day that measurements were made. Sets of measurements were taken at 15-min intervals until no significant change occurred.

Interfacial tension measurements. Measurements were made by the spinning drop technique using a model 500 spinning drop interfacial tensiometer (University of Texas). Readings were taken a 0.5-hr intervals until three

consecutive readings coincided. All readings were done at 25.0°C. The density of water was taken as 1.000 g/cm³ and that of n-hexadecane as 0.773 g/cm³.

Contact angle measurements. Advancing contact angles were measured with a contact angle goniometer (Model 100-00, Rame-Hart, Inc.). Four drops, each about 12 μ L, were applied to the solid surface, which was then placed in a thermostated environmental chamber (Model 100-07, Rame-Hart, Inc.) saturated with solution vapor to retard droplet evaporation. Angles were measured on both sides of each of the four drops. All measurements were made at least 30 min, and sometimes 1 hr after application of the drops. The temperature was 25 \pm 0.2°C. The advancing contact angle reproducibility was within 0.5–1.5°, depending upon the substrate and the surfactant.

Partition coefficient (C_H/C_W) of $C_{16}BGEO_5S$. Fifty ml of 2.70 \times 10⁻⁴M $C_{16}EO_5S$ in aqueous 0.1M NaCl were overlaid with 25ml of hexadecane and allowed to partition to equilibrium. The concentration of $C_{16}EO_5S$ in the aqueous phase was then determined by two phase titration with Hyamine, using mixed indicator. The partition coefficient was 0.037.

RESULTS AND DISCUSSION

Individual surfactants. Figure 1 shows surface tension (γ_{LV}) vs log molar concentration (C) plots for $C_{16}BGEO_5S$, $C_{16}LGEO_5S$, and LAS in 0.1M NaCl aqueous solution at 25.0°C. Figure 2 shows interfacial tension (γ_{LL}) vs log C_w curves in 0.1M NaCl aqueous solution/hexadecane systems (γ_{LL} is the aqueous solution/hexadecane interfacial tension and C_w is the molar concentration of the surfactant in the aqueous phase after partition). Figures 3 and 4 show adhesion tension $\gamma_{LV} \cos \theta$ (θ = contact angle) vs initial log C curves on Parafilm and Teflon, respectively.

Some interfacial properties of the compounds are listed in Table 1. Critical micelle concentrations (CMC) were taken as the concentrations at the point of intersection of

TABLE 1

Interfacial Properties of $C_{16}BGEO_5S$, $C_{16}LGEO_5S$ and LAS in Aqueous 0.1M NaCl at 25°C

Property	$C_{16}BGEO_5S$	$C_{16}LGEO_5S$	LAS
<i>0.1M NaCl (aq)/air</i>			
CMC ($M \times 10^5$)	3.3 ₂	1.1 ₆	16
Γ_{max} (mol/ $CM^2 \times 10^{10}$)	2.8 ₀	3.0 ₇	3.6 ₁
A_{min} (nm ² $\times 100$)	59 ₃	54 ₁	46 ₀
pC ₂₀ (pC ₃₀)	5.8 ₈ , (5.2 ₆)	6.1 ₉ , (5.6 ₃)	4.8 ₆
CMC/ C_{20} (CMC/ C_{30})	25 ₁ , (6.0)	18 ₀ , (4.9)	11 ₆
γ_{cmc} (mN/m)	29 ₅	30 ₂	30 ₄
Π_{cmc} (mN/m)	42 ₈	42 ₁	41 ₉
$-\Delta G_{ad}^{\circ}$ (KJ/mol)	68 ₃	69 ₂	50 ₂
<i>0.1M NaCl (aq)/Hexadecane</i>			
CMC ($M \times 10^5$)	3.8 ₀	1.0 ₅	
Γ_{max} (mol/ $KM^2 \times 10^{10}$)	3.2 ₉	3.2 ₃	
A_{min} (Å^2)	50 ₅	51 ₄	
pC ₃₀	5.5 ₀	6.0 ₆	
CMC/ C_{30}	11 ₉	11 ₉	
γ_{cmc} (mN/m)	2 ₀	2 ₅	
Π_{cmc} (mN/m)	50 ₄	49 ₉	
$-\Delta G_{ad}^{\circ}$ (KJ/mol)	67 ₉	71 ₂	
<i>0.1M NaCl (aq)/Parafilm</i>			
Γ_{max} (mol/ $CM^2 \times 10^{10}$)	3.5	5.7	4.5 ₆
A_{min} (Å^2)	47	29	36 ₄
pC ₂₀	5.3 ₄	5.0 ₂	4.6 ₆
Π_{max} (mN/m)	46 ₂	45 ₈	44 ₄
<i>0.1M NaCl (aq)/Teflon</i>			
Γ_{max} (mol/ $CM^2 \times 10^{10}$)	3.5	5.1	4.2 ₃
A_{min} (Å^2)	48	32	38 ₄
pC ₂₀	5.1 ₃	4.9 ₉	4.4 ₆
Π_{max} (mN/m)	39 ₁	40 ₇	39 ₁

the two linear portions of the γ_{LV} vs log C (or γ_{LL} vs log C_w) plots.

Maximum surface (or interfacial) excess concentration, Γ_{max} , in mol cm⁻², and minimum areas per surfactant molecule, A_{min} , in nm², at the aqueous solution/air (or

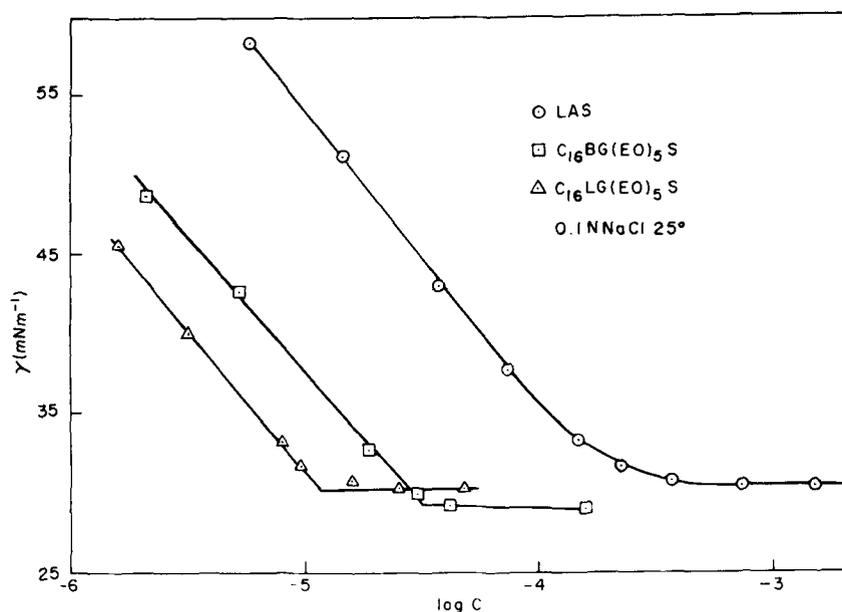


FIG. 1. Surface tension vs log molar concentration of \circ , LAS; \square , $C_{16}BGEO_5S$; and \triangle , $C_{16}LGEO_5S$ at 25°C in aqueous 0.1M NaCl.

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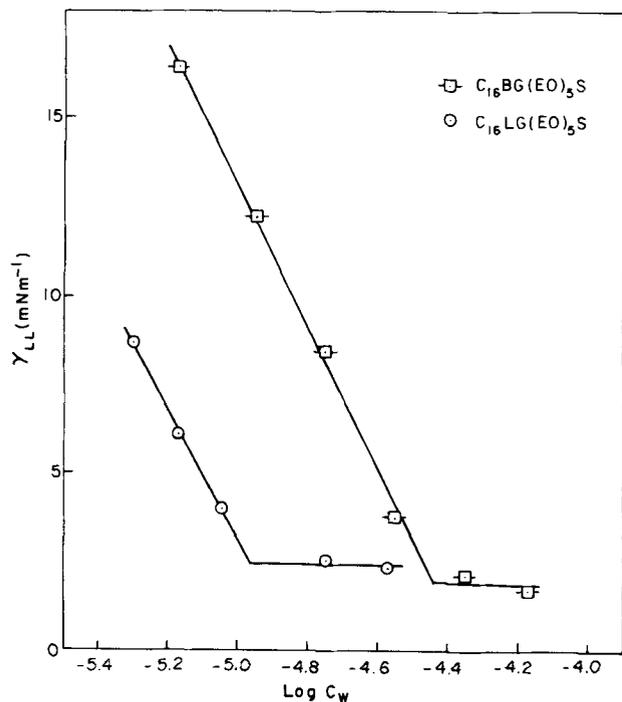


FIG. 2. Tension at the aqueous 0.1M NaCl/hexadecane interface vs log molar concentration in the aqueous phase of \square , $C_{16}BGEO_5S$ and \circ , $C_{16}LGEO_5S$ at 25°C.

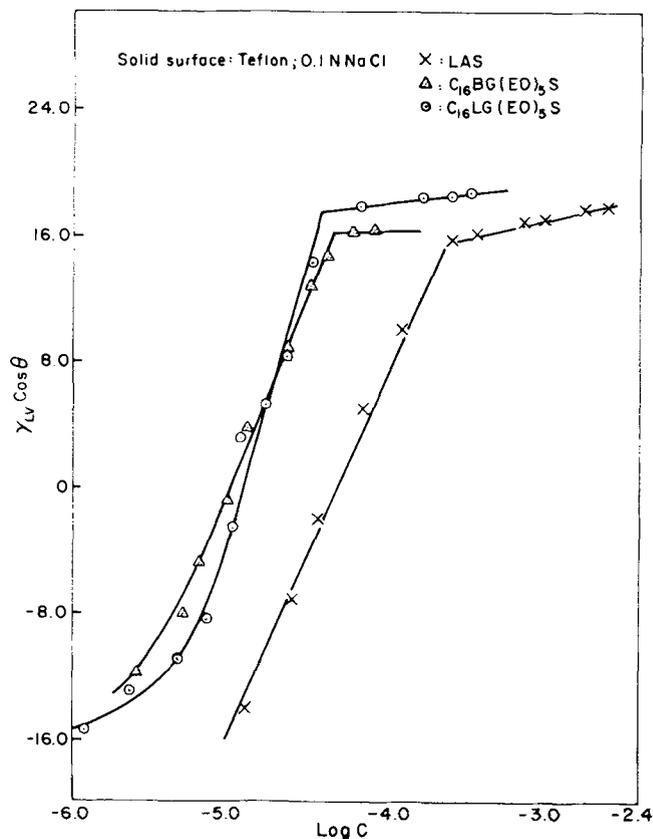


FIG. 4. Adhesion tension on Teflon vs log initial molar concentration of X, LAS; Δ , $C_{16}BGEO_5S$; and \circ , $C_{16}LGEO_5S$ at 25°C in aqueous 0.1M NaCl.

aqueous solution/hexadecane) interface were obtained from the maximum slopes (S_{max}) of the γ_{LV} vs $\log C$ (or γ_{LL} vs $\log C_w$) plots at 25°C by use of the Gibbs adsorption equation

$$-d\gamma = 2.303 RT d \log C, \quad [1]$$

from which

$$\Gamma_{max} = S_{max}/2.303 RT \quad [2]$$

$$A_{min} = 10^{14}/N\Gamma_{max} \quad [3]$$

where $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ and N is Avogadro's number.

Values of Γ_{max} at the aqueous solution/solid interfaces were obtained from the maximum slopes of $\gamma_{LV} \text{ Cos } \theta$ vs $\log C$ curves. From Young's equation

$$\gamma_{LV} \text{ Cos } \theta = \gamma_{SV} - \gamma_{SL} \quad [4]$$

where γ_{SV} and γ_{SL} are the tensions at the solid/vapor and solid/liquid interfaces, respectively. Since both Teflon and Parafilm are low-energy solids, it can be assumed that γ_{SV} is constant with change in the concentration of the surfactant in the aqueous phase. Therefore, from equations [1] and [4]

$$-d\gamma_{SL} = d(\gamma_{LV} \text{ Cos } \theta) = 2.303 RT \Gamma d \log C \quad [5]$$

From equation [5]

$$\Gamma_{max} = \frac{1}{2.303 RT} \frac{d\gamma_{LV} \text{ Cos } \theta}{d \log C} \quad [6]$$

A_{min} values are then obtained by equation [3].

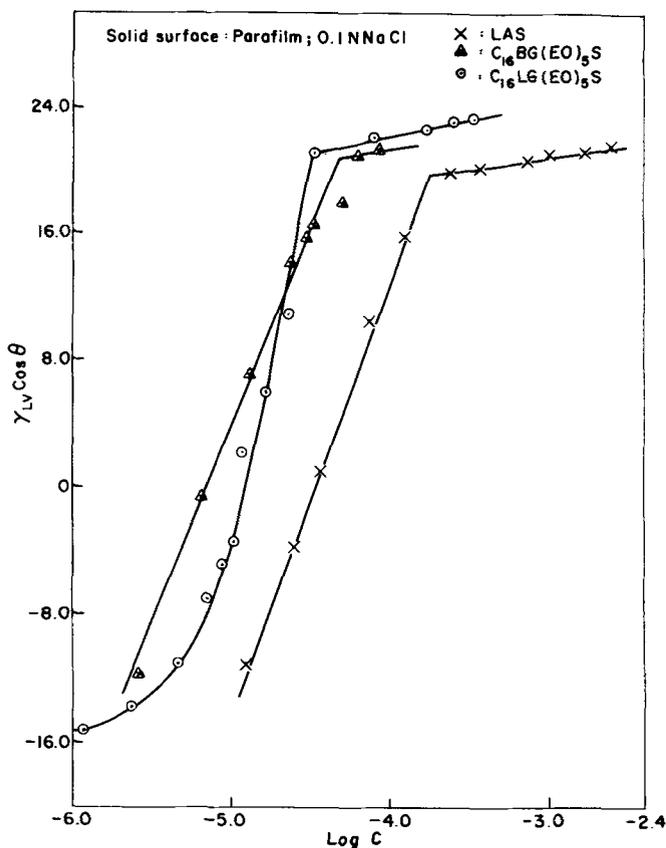


FIG. 3. Adhesion tension on Parafilm vs log initial molar concentration of X, LAS; Δ , $C_{16}BGEO_5S$; and \circ , $C_{16}LGEO_5S$ at 25°C in aqueous 0.1M NaCl.

The pC_{20} value, the negative log of the molar concentration of surfactant required to produce a 20 mN/m reduction in surface or interfacial tension or a 20 mN/m surface pressure $\Pi (= \gamma^0 - \gamma)$, where γ^0 is the surface or interfacial tension in the absence of the surfactant), is a measure of the surface or interfacial tension reduction efficiency of the surfactant. From equation [3], the solid/liquid interfacial tension in the absence of the surfactant, γ^0_{SL} , is given by the expression

$$\gamma^0_{SL} = \gamma^0_{SV} - \gamma^0_{LV} \cos \theta^0 \quad [7]$$

where γ^0_{SL} , γ^0_{LV} , and θ^0 are the values in the absence of the surfactant. From equations [4] and [7]

$$\gamma^0_{SL} - \gamma_{SL} = \Pi^0_{SL} = \gamma^0_{SV} - \gamma_{SV} - \gamma^0_{LV} \cos \theta^0 + \gamma_{LV} \cos \theta \quad [8]$$

Since the solid/vapor interfacial tension for Teflon and Parafilm surfaces can be assumed to be constant, the pC_{20} value can be taken from the $\gamma_{LV} \cos \theta$ vs $\log C$ plot at the point where $\gamma_{LV} \cos \theta = \gamma^0_{LV} \cos \theta^0 + 20$. Since surface tension and contact angle measurements of the 0.1M aqueous solution used at 25°C yield $\gamma^0_{LV} \cos \theta^0$ values of -24.4 and -23.1 mN/m for Parafilm and Teflon, respectively, the corresponding $\gamma_{LV} \cos \theta$ values for obtaining pC_{20} are -4.4 and -3.1 mN/m.

The CMC/ C_{20} ratio is a convenient way of measuring the relative effects of some structural or microenvironmental factor on micellization and adsorption. An increase in the CMC/ C_{20} ratio as a result of the introduction of some factor indicates that micellization is inhibited more than adsorption, or that adsorption is facilitated more than micellization; a decrease in the CMC/ C_{20} ratio indicates that adsorption is inhibited more than micellization, or that micellization is facilitated more than adsorption.

The surface or interfacial tension of the surfactant system at the CMC is γ_{cmc} . $\Pi_{cmc} (= \gamma^0 - \gamma_{cmc})$ is the surface or interfacial pressure at the CMC. From equation [8], $\Pi_{max} [= -\gamma^0_{LV} \cos \theta^0 + (\gamma_{LV} \cos \theta)_{max}]$ values at the solid/liquid interface were calculated from the expression

$$\Pi_{max} = 24.4 + (\gamma_{LV} \cos \theta)_{max} \quad [9]$$

for Parafilm and

$$\Pi_{max} = 23.1 + (\gamma_{LV} \cos \theta)_{max} \quad [9a]$$

for Teflon

Standard free energies of adsorption were calculated from the relationship (4)

$$\Delta G^0_{ads} = RT [\ln(C_s^-/\omega) + \ln f_- + \ln(C_x^+/\omega) + \ln f_+] - 6.023 \times 10^{-1} \Pi \cdot A_{min} \quad [10]$$

for these surfactants in swamping amount of common-ion containing electrolyte. Here, the standard state for the surface (or interfacial) phase is a hypothetical monolayer of the surfactant at its closest packing ($A = A_{min}$), but at a surface pressure of zero. $R = 0.00834$ KJ/mol, T is in °K, C_s^- is the molar concentration of surfactant, f_- is its activity coefficient, C_x^+ is the molar concentration of the counter-ion, f_+ is its activity

coefficient, ω is the molar concentration of water (55.3 at 25°C), A_{min} is in nm^2 , Π in mN/m is at any value where $A = A_{min}$, and ΔG^0_{ads} is in KJ/mol. The activity coefficients f_- and f_+ can be approximated using the extended Debye-Hukhel equation (5):

$$\log f = -B (I)^{1/2} / [1 + 0.33 \alpha (I)^{1/2}] \quad [11]$$

where I is the total ionic strength of the solution, B is 0.509 at 25.0°C, and α is taken as 0.3 for the Na^+ ions and 0.6 for the surfactant ion.

Properties for the aqueous solution/air systems. The properties of the three investigated materials at the aqueous solution/air interface all indicate that the carbon equivalency of the hydrophobic group (and hence the hydrophobic character) of $C_{16}LGEO_5S$ (the "L isomer") is greater than that of $C_{16}BGEO_5S$ (the "B isomer") and that both have a much greater carbon equivalency than LAS. This is consistent with previous data showing that the insertion of oxyethylene groups between the hydrophobic group and an ionic hydrophilic group results in increased hydrophobic character in the molecule (6) and that branched hydrophobic groups have lower carbon equivalencies than isomeric straight chain groups (7). Thus, the cmc value increases, the pC_{20} value decreases, and the ΔG^0_{ad} value becomes less negative in the order: L isomer - B isomer - LAS.

As the degree of branching in the hydrophobic tail increases, micellization is inhibited relative to adsorption, due to the more rigid packing requirement in the case of the micelle than at the planar interface, where there is more conformational freedom. Thus the cmc/ C_{20} (or cmc/ C_{30}) ratio increases in the order: LAS < L isomer < B isomer. The greater steric inhibition of micellization by the highly branched B isomer also accounts for its slightly lower γ_{cmc} (higher Π_{cmc}) value than for the L isomer or for LAS.

The maximum surface excess concentration, Γ_{max} , and the corresponding minimum area per molecule, A_{min} at the aqueous/air interface reflect both the greater branching of the B isomer relative to the L isomer and the larger cross-sectional area of a molecule containing a polyoxyethylene group. Thus A_{min} increases in the order: LAS << L isomer < B isomer.

The free energies of adsorption of the B and L isomers are almost equal. The larger number of $-CH_3$ groups in the hydrophobic group of the B isomer, with their larger contribution (8,9) than the $-CH_2$ group to the $-\Delta G^0_{ad}$ value, apparently compensates for the larger carbon equivalency of the L isomer.

Properties for the aqueous solution/hexadecane systems. When air is replaced by hexadecane for surfactants that do not partition significantly into the hexadecane, there is only a small change in the interfacial properties, in agreement with the findings of Rehfeld (10) and Murphy and Rosen (11). For these ionic surfactants in a swamping amount of NaCl in the aqueous phase, head group repulsions are reduced and the presence of hexadecane results in compression of the interfacial film, as measured by A_{min} , relative to that at the L/A interface. This is probably the result of the interaction of the hydrophobic tails with hexadecane molecules. Both isomers reduce the interfacial tension to relatively low values as measured by γ_{min} . The

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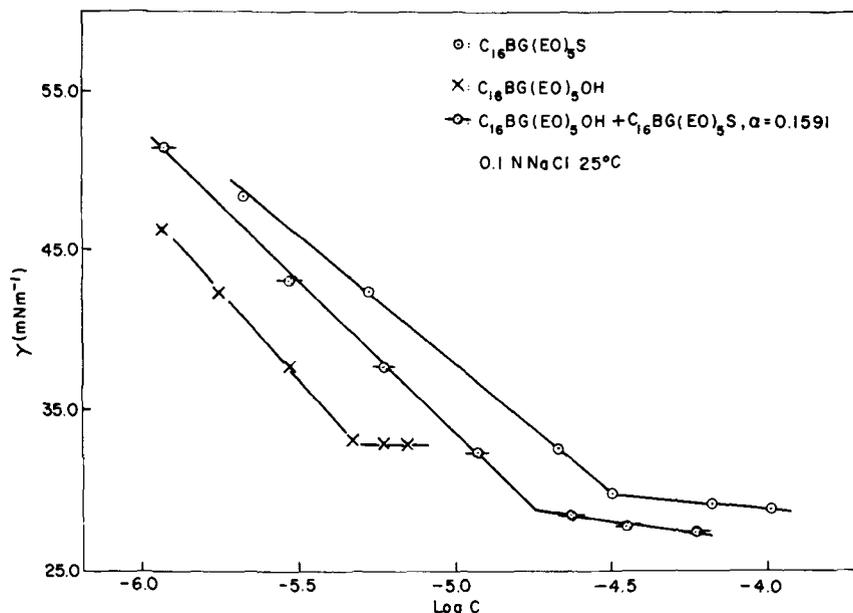


FIG. 5. Surface tension vs log molar concentration of \odot , $C_{16}BGEOS$; \times , $C_{16}BGEOSOH$; and their mixture, \ominus , at $\alpha_{alcohol}=0.159$ at $25^{\circ}C$ in aqueous $0.1M NaCl$.

increase in the value of Π_{cmc} relative to the L/A case is due to the larger pC_{20} and CMC/c_{30} values, as found previously (11).

Properties for the aqueous solution/low-energy solid systems. When air is replaced by Teflon or Parafilm, the interfacial properties of these surfactants are considerably affected. The area per molecule values are greatly reduced compared to the corresponding L/A values, and may indicate multilayer adsorption at the aqueous solution/solid interfaces. This effect is more pronounced for the L isomer on both of the solids investigated. ΔG_{ad}^0 values are based on monolayer adsorption and therefore have not been included.

Both the B and L isomers are much more efficient at reducing contact angle on both solids than LAS. In order to reach a contact angle of 46° on Parafilm, $1 \times 10^{-3}M$ LAS is needed, but only $4.7 \times 10^{-5}M$ B and $3.1 \times 10^{-5}M$ L isomer. In order to reach a contact angle of 56° on Teflon, $9 \times 10^{-4}M$ LAS is needed, but only $6 \times 10^{-5}M$ B isomer and $5 \times 10^{-5}M$ L isomer.

Binary surfactant mixtures. Figure 5 shows the surface tension vs log molar concentration plots for $C_{16}BGEOS$, $C_{16}BGEOSOH$, and their mixture in $0.1M NaCl$ aqueous solution at $25^{\circ}C$. Figure 6 shows interfacial tension vs log total concentration plots for $C_{16}BEO_5S$, $C_{16}BEO_5OH$, a mixture of them, and $C_{16}LEO_5S$, $C_{16}LEO_5OH$, and a mixture of them.

Table 2 lists interaction and synergism parameters for the mixtures investigated. Following previous publications (12,13), values of β^{σ} , the interaction parameter for the two surfactants at the aqueous/air interface, were calculated by use of equations [12] and [13].

$$\frac{X_1^2 \ln(\alpha_1 C_{12}/X_1 C_1^0)}{(1-X_1)^2 \ln[(1-X_1) C_{12}/(1-X_1) C_2^0]} = 1 \quad [12]$$

Equation [12] is first solved iteratively for X_1 , where X_1 is the mole fraction of surfactant 1 in the total surfactant at the aqueous solution/air interface; α is the mole fraction

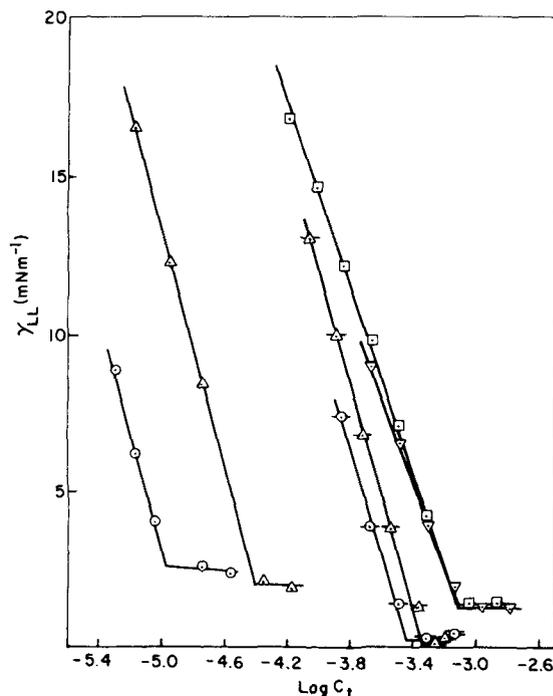


FIG. 6. Tension at the aqueous $0.1M NaCl$ /hexadecane interface vs log total molar concentration in the system at $25^{\circ}C$ for \odot , $C_{16}LGEOS$; Δ , $C_{16}BGEOS$; \ominus , $C_{16}LGEOS/C_{16}LGEOSOH$ mixture, $\alpha_{sulfate}=0.013$; ∇ , $C_{16}BGEOS/C_{16}BGEOSOH$ mixture, $\alpha_{sulfate}=0.012$; \square , $C_{16}LGEOSOH$.

of surfactant 1 in the total surfactant in the aqueous solution; and C_1^0 , C_2^0 and C_{12} are the solution phase molar concentration of surfactants 1 and 2 and their mixture, respectively, required to produce a given surface tension value. Then X_1 is substituted into equation [13]

$$\beta^{\sigma} = \frac{\ln(\alpha_1 C_{12}/X_1 C_1^0)}{(1-X_1)^2} \quad [13]$$

TABLE 2

Molecular Interaction and Synergism Parameters for Binary Surfactant Mixtures at 25°C

Parameter	C ₁₆ BGEO ₅ S + C ₁₆ BGEO ₅ OH	C ₁₆ LGEO ₅ S + C ₁₆ LGEO ₅ OH
<i>0.1M NaCl (aq.)/air</i>		
mole fraction of anionic	0.84	
β^σ	-1.1	
$ \ln C_1^\circ/C_2^\circ $	1.6	
β^M	+0.4	
$ \ln(\text{CMC}_1/\text{CMC}_2)$	1.9	
$\beta^\sigma - \beta^M$	-1.5	
$C_1^\circ \text{CMC}_2^\circ$	0.33	
$ \ln \frac{C_2^\circ \text{CMC}_1^\circ}{C_1^\circ \text{CMC}_2^\circ} $		
$\alpha_{\text{sulfate}}^{\cdot E}$	0.91	
Mixture γ_{cmc} (dynes/cm)	28.2	
Lowest individual γ_{cmc} (dynes/cm)	29.2	
<i>0.1M NaCl (aq.)/Hexadecane</i>		
Mole fraction of anionic in the entire system	0.012 ₉	0.013 ₈
Mole fraction of anionic in aq. phase (after partitioning of nonionic)	0.8	0.9 ₅
β_{LL}^σ	-2.2	-1.2
$C_{1,t}^\circ$		
$ \ln \frac{C_{2,t}^\circ}{C_{1,t}^\circ} $	2.9	4.1
β_{LL}^M	-1.5	-0.2
$\text{CMC}_{1,t}$	3.0	4.3
$ \ln \frac{\text{CMC}_{2,t}}{\text{CMC}_{1,t}} $		
$\beta^\sigma - \beta^M$	-0.7	-1.0
$C_{1,t}^\circ \text{CMC}_{2,t}$	0.1	0.2
$ \ln \frac{C_{2,t}^\circ \text{CMC}_{1,t}}{C_{1,t}^\circ \text{CMC}_{2,t}} $		
$\alpha^{\cdot E} \text{sulfate}$	$3.6_5 \times 10^{-2}$	9.8×10^{-3}
Mixture $\gamma_{\text{I,cmc}}$ (dynes/cm)	0.10	0.13
Lowest individual $\gamma_{\text{I,cmc}}$ (dynes/cm)	1.3	1.4

in order to obtain β^σ , the molecular interaction parameter between surfactants 1 and 2 at the aqueous solution/air interface. Negative β^σ values indicate attractive interaction, positive values indicate repulsive interaction.

For determining β^M , the interaction parameter for mixed micelles of the two surfactants, equation [12] is solved for X^M , the mole fraction of surfactant 1 in the total surfactant in the mixed micelle, using the corresponding critical micelle concentrations instead of C_1° , C_2° and C_{12} . This is inserted in equation [13] to calculate β^M .

For measuring β_{LL}^σ , the molecular interaction parameter at the liquid/liquid interface, equation [14] is first iteratively solved for $X_{1,l}$, where $X_{1,l}$ is the mole fraction of surfactant

$$\frac{(X_{1,l})^2 \ln(F_1 C_{12,t} \alpha_1 / F_1^\circ C_{1,t}^\circ X_{1,l})}{(1 - X_{1,l})^2 \ln[F_2 C_{12,t} (1 - \alpha) / F_2^\circ (C_{2,t}^\circ (1 - X_{1,l}))]}, \quad [14]$$

1 in the total surfactant at the aqueous solution/hydrocarbon interface; $F_1 = (\phi + 1)/(K\phi + 1)$ is the fraction of surfactant 1 in the aqueous phase of the surfactant mixture; $F_2 = (\phi + 1)/(K_2\phi + 1)$ the fraction of surfactant 2 in the aqueous phase of the surfactant mixture; $F_1^\circ = (\phi_1^\circ +$

$1)/(K_1\phi_1^\circ + 1)$ the fraction of surfactant 1 in the aqueous phase of the system containing only surfactant 1; and $F_2^\circ = (\phi_2^\circ + 1)/(K_2\phi_2^\circ + 1)$ the fraction of surfactant 2 in the aqueous phase of the system containing only surfactant 2. The nonaqueous/aqueous phase volume ratio is ϕ and K the nonaqueous/aqueous molar partition coefficient of each surfactant. $C_{1,t}^\circ$, $C_{2,t}^\circ$ and $C_{12,t}$ are the concentrations, based upon the total volume of the system, required to produce the same interfacial value. Once $X_{1,l}$ is known, it is substituted in equation [15]

$$\beta_{\text{LL}}^\sigma = \frac{\ln(C_{12,t} \alpha_1 F_1 / F_1^\circ C_{1,t}^\circ X_{1,l})}{(1 - X_{1,l})^2} \quad [15]$$

in order to obtain β_{LL}^σ , the molecular interaction parameter between surfactants 1 and 2 at the aqueous solution/hydrocarbon interface.

When α_1 approaches zero or one, the partition coefficient values may be eliminated from equations [14] and [15] since in the limit $\alpha_1 \rightarrow 1$, $\alpha_1 C_{12,t} \rightarrow C_{1,t}^\circ$, $k_1 \rightarrow k_1^\circ$, and $F_1^\circ / F_1 \rightarrow 1$, and in the limit $\alpha_1 \rightarrow 0$, $F_1^\circ / F_1 \alpha_1 \rightarrow 0$ and the effect of F_1° / F_1 on $X_{1,l}$ and β_{LL}^σ becomes negligible. Similar relationships hold for α_2 . Since these conditions are met in the systems investigated here, equations [14] and [15] without F_1° , F_1 , F_2 or F_2° were used to calculate $X_{1,l}$ and β_{LL}^σ . $C_{1,t}^\circ$, $C_{2,t}^\circ$ and $C_{12,t}$ are the concentrations, based upon the total volume of the system, required to produce the same interfacial tension value.

Equations analogous to equations [14] and [15] without F_1 , F_2 , F_1° and F_2° hold for the calculation of β_{LL}^M , the mixed micellar molecular interaction parameter between surfactants 1 and 2 in aqueous solution/hydrocarbon systems.

The mole fraction at the point of maximum synergism in surface tension reduction effectiveness is given by the relationship (14):

$$\alpha_1^{\cdot E} = [((\text{CMC}_1^\circ / \text{CMC}_2^\circ) \cdot (X_1' / (1 - X_1'))) \times \exp \beta^M (1 - 2X_1') / \{1 + [((\text{CMC}_1^\circ / \text{CMC}_2^\circ) \times (X_1' / 1 - X_1')) \exp \beta^M (1 - 2X_1')]\}] \quad [16]$$

where X_1' is the mole fraction of surfactant 1 at the surface at the point of maximum and is calculated iteratively from equation [16]

$$\frac{\gamma_{\text{cmc}1}^\circ - S_1 (\beta^\sigma - \beta^M) (1 - X_1')^2}{\gamma_{\text{cmc}2}^\circ - S_2 (\beta^\sigma - \beta^M) (X_1')^2} = 1, \quad [17]$$

where $\gamma_{\text{cmc}1}^\circ$ and $\gamma_{\text{cmc}2}^\circ$ are the surface tension values at their CMC's of individual surfactants 1 and 2, respectively; and S_1 and S_2 are the slopes of the $\gamma - \ln C$ plots of the individual surfactants 1 and 2, respectively.

Since for the aqueous solution/hydrocarbon systems investigated, α tends toward zero, partition coefficients are not needed to calculate $\alpha_1^{\cdot E}$. Equations analogous to [16] and [17], but based on concentrations in the entire system and upon interfacial tensions are used to calculate $\alpha_1^{\cdot E}$ for the liquid/liquid systems.

Aqueous solution/air system. The C₁₆BGEO₅S - C₁₆LGEO₅OH mixture showed only weak interaction between the two surfactants, both in mixed monolayer ($\beta^\sigma - 1.1$) and in mixed micelle ($\beta^M = +0.4$) formation. The

rather weak interactions between the surfactants are probably due to the highly branched alkyl chains preventing the close approach of the two surfactants. Such weak interactions are also seen in mixtures of sodium di-(2-ethylhexyl) sulfosuccinate (15) another highly branched surfactant, with the nonionic surfactant, $C_{12}H_{25}(EO)_5OH$ ($\beta, \sigma - 0.9$; $\beta, M - 1.2$). Since the condition for synergism in surface tension reduction efficiency (16) is $|\beta^\sigma| > |\ln(C_1^\circ/C_2^\circ)|$ and the condition for synergism in mixed micelle formation is $|\beta^M| > |\ln(CMC_1/CMC_2)|$, the data in Table 2 indicate that these conditions are not met and these two types of synergism are not observed in mixtures of these two materials.

However, synergism in surface tension reduction effectiveness (14) is shown by this mixture since the condition for synergism, in this respect,

$$|\beta^\sigma - \beta^M| > \left| \ln \frac{C_1^\circ CMC_2^\circ}{C_2^\circ CMC_1^\circ} \right|,$$

is attained. As a result, the mixture depresses the surface tension to a value (28.2 dynes/cm) lower than that attainable by either component by itself. The $\alpha^{*E}_{sulfate}$ value is calculated to be 0.91.

Aqueous solution/hydrocarbon systems. Both the $C_{16}BGEO_5S - C_{16}BGEO_5OH$ and $C_{16}LGEO_5S - C_{16}LGEO_5OH$ mixtures show synergism in interfacial tension reduction effectiveness, while showing no synergism in interfacial tension reduction efficiency or mixed micelle formation. Because of the synergism in interfacial tension reduction effectiveness, both these mixtures reduce the interfacial tension to less than 0.2 dynes/cm. The $\alpha^{*E}_{sulfate}$ value for the $C_{16}BGEO_5S - C_{16}BGEO_5OH$ mixture is calculated to be $3.6_5 \times 10^{-2}$, and the value for the $C_{16}LGEO_5S - C_{16}LGEO_5OH$ mixture is calculated to be 9.8×10^{-3} . The reason these $\alpha^{*E}_{sulfate}$ values are so much smaller than

for the L/A system is that in equation [15], when $CMC^\circ_{1,t} \ll CMC^\circ_{2,t} \alpha_1^{*E} - 0$, $C_{16}BGEO_5OH$ and $C_{16}LGEO_5OH$ are very oil soluble, which makes $CMC^\circ_{sulfate,t} \ll CMC^\circ_{alcohol,t}$ and therefore $\alpha^{*E}_{sulfate}$ to be very small for the L/L systems.

The value for the mole fraction of anionic in the aqueous phase after partitioning of the nonionic listed in Table 2 is obtained by assuming that the presence of hexadecane does not appreciably affect the CMC in the aqueous phase, and using the difference between the CMC in the aqueous solution/air system and the CMC for the total system in the aqueous solution/hexadecane case to calculate approximate partition coefficient values: $C_{16}BGEO_5OH, K (=C_0/C_w) \approx 7 \times 10^3$; $C_{16}LGEO_5OH, K \approx 2 \times 10^4$.

Draves wetting. Draves wetting times are listed in Table 3. At all concentrations investigated, the order of wetting time at a fixed surfactant concentration was B isomer $< LAS < L$ isomer. The B isomer, which is the most highly branched material and also reaches the lowest surface tension, is the best wetting agent.

Data on the $C_{16}BGEO_5S - C_{16}BGEO_5OH$ mixture indicate that, in contrast to the situation in surface and interfacial tension lowering where the performance of $C_{16}BGEO_5S$ was improved by the addition of $C_{16}BGEO_5OH$, such improvement does not extend to wetting.

Ross-Miles foaming. Ross-Miles Foaming data are listed in Table 4. Effectiveness in foaming is measured by the initial foam height. From the data, $C_{16}BGEO_5S$ and LAS are about equally effective, while $C_{16}LGEO_5S$ is significantly less effective.

Foam stability can be measured by dividing the foam height at five minutes by the initial height. The stabilities of all three pure compounds at the concentrations investigated are comparable, with LAS and $C_{16}LGEO_5S$ producing a slightly more stable foam than $C_{16}BGEO_5S$. The addition of $C_{16}BGEO_5OH$ to $C_{16}BGEO_5S$ decreases both the foaming effectiveness and foam stability of the latter.

TABLE 3

Draves Wetting Times (sec), 0.1M NaCl

Concentration (% w/w)	$C_{16}BGEO_5S$ 24.5°C	$C_{16}LGEO_5S$ 27°C	LAS 27°C	$C_{16}BGEO_5S + C_{16}LGEO_5OH$ $\alpha_{nonionic}=0.1, 29^\circ C$
0.10	6.9	12.4	8.0	8.6
0.05	14.4	25.6	17.1	—
0.025	39.9	61.6	58.5	—

TABLE 4

Ross-Miles Foaming, 60°C, 0.1M NaCl

Concentration (% w/w)	$C_{16}BG(EO)_5S$		$C_{16}LGEO_5S$		LAS		$C_{16}BG(EO)_5S + C_{16}BGEO_5OH$ $\alpha_{nonionic}=0.1$	
	Initial foam height (mm)	5 min Stability	Initial foam height (mm)	5 min Stability	Initial foam height (mm)	5 min Stability	Initial foam height (mm)	5 min Stability
0.25	200	0.93	174	0.97	200	0.95	190 ^a	0.83 ^a
0.10	199	0.93	165	0.96	—	—	157	0.89
0.025	170-180	≈0.90	147	0.97	191	0.98	—	—

^aSolution cloudy.

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