Surface Activity of Mixtures of Dodecyl Trimethyl Ammonium Bromide with Sodium Perfluorooctanoate and Sodium Octanoate

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ABSTRACT: In this study, the surface tension of mixtures of cationic surfactant dodecyl trimethylammonium bromide (DTAB) and anionic surfactant sodium perfluorooctanoate (SPFO) was evaluated as a function of DTAB-SPFO composition and total surfactant concentration, with and without added electrolyte. It was found that the critical micelle concentration (CMC) of these mixtures was reduced by more than two orders of magnitude when compared to the CMC of SPFO and DTAB alone. The surface tension, after CMC, of the mixtures was close to that of SPFO with added electrolyte and even lower than that of SPFO without added electrolyte. Using the appropriate combination of SPFO and DTAB, surface tensions near 18 mJ/m^2 were obtained using a concentration 1/500 of that required for SPFO alone. When these results were compared to those obtained for DTAB-sodium octanoate (SOCT) mixtures, it was evident that the DTAB-SPFO system shows a larger degree of synergism than the DTAB-SOCT system. Contact angle measurements on Teflon® surfaces corroborates that the lower surface tension of DTAB-SPFO mixtures improves wetting on these hydrophobic surfaces. Using the regular solution theory to interpret the data of CMC and C45mJ/m^2 (monolayer formation) versus DTAB-SPFO composition, it was concluded that even when small concentrations of SPFO are introduced in the mixture, the composition of the micelles (at the CMC) and monolayer adsorbed at the air-water interface tends to be equimolar in SPFO and DTAB.

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KEY WORDS: mixtures, anionic, cationic, anionic-cationic, ion-pair, regular solution, fluorocarbons, surface tension.

Surfactants play an important role in our everyday life. They are essential ingredients in many consumer products and industrial processes that range from laundry detergency to mineral flotation, to nanoparticle synthesis. Recent statistics reported by Scheibel (1), reveal that in the year 2000 the global market for detergents was $60 billion per year, and the worldwide surfactant consumption was close to 22 billion pounds per year (1). To reduce costs and the environmental impact of surfactants, the surfactant and detergent industry is looking for ways of reducing the concentration of surfactants in the different formulations without compromising the performance characteristics. This trend is even more accelerated for the case of fluorocarbon-based surfactants (also called fluorinated surfactants) due to their poor biodegradability and their tendency to bioaccumulate.

Fluorinated surfactants are currently used because of their exceptional surface activity. These surfactants can reduce the surface tension of water from 72 mN/m (at 25°C) to values close to 20 mN/m, a value which is much lower than the surface tension reached with hydrocarbon-based surfactants (~35 mN/m) (2). Fluorinated surfactants exhibit surface activity even in organic systems and are stable to heat, acids and bases, and reducing and oxidizing agents (2,3). Typically, fluorocarbon surfactants are used as anti-fogging, cleaning, wetting, dispersing, emulsifying, foaming/defoaming, and floating agents (3). Fluorocarbon surfactants are used in various products, such as coatings, cosmetics, electronics, paper, plastics, and textiles (3).

Fluorinated surfactants cost typically about 10 times more than silicone-based surfactants and 100 times more than hydrocarbon-based surfactants (3). The relatively high price of fluorinated surfactants limits their use to applications where hydrocarbon-based surfactants are inadequate. However, fluorinated surfactants can reach low surface tension values using 1/10 of the concentration needed for silicones and about 1/50 of the concentration needed for hydrocarbon surfactants (3). Another downside of fluorinated surfactants is that some of them are toxic (cationic fluorinated surfactants, which are now banned in most parts of the world), while all of them are either poorly biodegradable or nonbiodegradable, and tend to bioaccumulate. Currently, the environmental and health impacts of perfluorooctanoic acid (used to produce Teflon®) are under intense review by the U.S. Environmental Protection Agency (USEPA).

Considering the relevance of fluorinated surfactants to today's coating, polymer, and cleaning products industry, it is necessary to find alternative formulations that can reproduce the surface activity of fluorinated surfactants using lower concentrations of these surfactants. This is the central topic of this work.

Surface activity of mixtures of anionic and cationic surfactants. The literature offers some ideas for improving the efficiency of

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fluorocarbon surfactants by introducing mixtures of anionic (negatively-charged) fluorocarbon surfactants with cationic (positively-charged) hydrocarbon-based surfactants. In particular, systems containing the anionic fluorinated surfactant such as sodium perfluoro-octanoate (SPFO) and hydrocarbon-based cationic surfactants such as octyl-trimethyl-ammonium-bromide (OCTAB) can produce low surface-tension values (~15 mJ/m^2) at lower total surfactant concentrations (4,5,6,7). This special synergism between anionic/cationic fluorinated and hydrocarbon surfactants contrasts with the segregation (demixing) behavior observed for mixtures of fluorocarbon and hydrocarbon surfactants with the same charge or of nonionic character (8,9,10). The strong synergism between anionic fluorinated surfactant and cationic hydrocarbon surfactants is also evidenced by their tendency to form rigid/viscous structures (vescicles, liquid crystals, and coacervates), which reflect the rigidity of such films (4,7,11).

The rigid/viscous structures mentioned above cause problems in most formulations. Thus, the mixed anionic-cationic surfactant approach has been abandoned since the early 1990s. As will be seen later, the problem with these initial studies is that they used surfactants with similar tail lengths (6 to 8 carbons) that, upon mixing at near equimolar ratios, induce the formation of liquid crystals, precipitate, coacervates, gels, and other undesirable phases. Doan *et al.* suggest that when mixing anionic and cationic surfactants, the best way to reduce the formation of gels and liquid crystals is through the introduction of "dissimilar" tail geometries in the mixtures, and by using mixing ratios other than equimolar compositions (12).

Thermodynamics of mixed surfactant systems—regular solution theory. In mixed surfactant systems, the interaction among surfactants may be synergistic (e.g., between anionic and cationic surfactants) or antagonist (e.g., between fluorocarbons and hydrocarbons of the same charge). The regular solution theory serves as a mathematical framework to evaluate the interaction in binary surfactant mixtures. This interaction is assessed through a molecular interaction parameter, β (13). In short, the regular solution theory considers micelles to be a surfactant pseudophase in equilibrium, with surfactant monomers in solution. Using similar expressions to those used in vapor-liquid equilibrium, for a binary mixture of surfactants A and B we obtain the following (13):

$$Y_A CMC = CMC_A = X_A CMC_A^o EXP[\beta(1 - X_A)^2] \quad [1]$$

$$(1 - Y_A) CMC = CMC_B = (1 - X_A) CMC_B^o EXP(\beta X_A^2) \quad [2]$$

where CMC is the critical micelle concentration of the mixture, CMC_A° and CMC_B° are the pure surfactant-critical micelle concentrations of A and B, respectively. X_A is the mole fraction of surfactant A in the micellar pseudophase, and Y_A is the mole fraction of component A in the monomer pseudophase ($Y_A = CMC_A/[CMC_A + CMC_B]$). In these expressions the Margules 1-parameter (β) model is used to calculate the activity coefficients in the micellar pseudophase.

In practice, the CMC of a mixture of known Y_A is obtained experimentally (e.g., through surface tension measurements). Using the same procedure, the pure component CMCs (CMC_A^o, CMC_B^o) are obtained. To calculate the values of β and X_A, Equations 1 and 2 are solved simultaneously. Often swamping electrolyte concentrations are used to prevent changes of pure-component CMCs with mixture composition or concentration.

Guo *et al.* (5) reported that for the SPFO-OCTAB (octyl-trimethylammonium bromide) mixed system, the synergistic nature of the mixture (negative β) induced the CMC to drop by up to two orders of magnitude (compared to the CMC of OCTAB). They also found that the surface tensions of pure SPFO and OCTAB after CMC were 22 and 46 mJ/m^2, respectively, while the surface tension of the mixed system was found to be 14–15 mJ/m^2 and almost independent of composition. When both fluorocarbon and hydrocarbon surfactants are anionic, the mixed systems, however, show strong positive deviations from ideal behavior (positive β) due to the repulsion between fluorocarbon and hydrocarbon chains (5).

Besides monomers and micelles, mixtures of anionic and cationic surfactants may yield other types of phases, such as liquid crystals and solid precipitate. The concentration of cationic surfactant required to precipitate an anionic surfactant (or vice versa) is shown to increase above the critical micelle concentration of the system (14). The monomer-precipitate equilibrium is modeled by a simple solubility product (15,16):

$$K_p = [AS^-] \cdot [CS^-] \quad [3]$$

where K_p is the solubility product of the complex, $[AS^-]$ is the monomer concentration of the anionic surfactant, and $[CS^-]$ is the cationic surfactant monomer concentration. Equation 2 ignores the activity coefficients in solution, which can be included for increased accuracy (15). At high surfactant concentrations, and as the mixture approaches equimolar concentrations of the cationic and anionic surfactant, a fraction of the micelle region becomes liquid crystalline. Despite some initial attempts, the micelle-liquid-crystal equilibrium has not been successfully modeled or predicted (17).

The monomer-micelle-precipitate equilibrium is found when combining Equations 1 and 2 (monomer-micelle) with Equation 3 (monomer-precipitate: $CMC_A CMC_B = Kp$). For a given interaction parameter, β, the solution of these three equations yields CMC_A^*, CMC_B^*, and X_A^*. (The asterisk indicates the monomer-micelle-precipitate equilibrium.) The surfactant mass balance in micelles and in monomers produces the phase boundary line:

$$C_A^* = CMC_A^* + [X_A^*/(1 - X_A^*)](C_B^* - CMC_B^*) \quad [4]$$

where C_A^* and C_B^* are the total surfactant concentration of species A and B that belong to the monomer-micelle-precipitate boundary line.

Equations 1 through 4 will be used in this work to evaluate the degree of interaction experienced by these systems

and estimate the compositions of micelles and monolayers, and predict the precipitation phase maps.

The working hypothesis for this work is that by introducing mixtures of anionic fluorinated surfactant and cationic hydrocarbon-based surfactants with dissimilar tail lengths, and using non-equimolar molar compositions, it will be possible to reproduce the surface activity of pure fluorinated surfactant while avoiding undesirable phases. To test this hypothesis, surfactant sodium perfluorooctanoate (SPFO) is used as the fluorinated surfactant. Sodium octanoate (SOCT) is used as a benchmark to compare the interaction between hydrocarbon-fluorocarbon, and hydrocarbon-hydrocarbon pairs.

The selection of the cationic surfactant to be used is also of great importance. There are examples of dissimilar tail-length systems that form insoluble phases, such as those formulated with (C8) SPFO and (C16) cetyltrimethylammonium bromide (CTAB) (7,18). This is consistent with Rubing's observation that, in order to avoid undesirable phases, mixtures of anionic and cationic surfactants should be limited to 20 carbons (when one adds the number of carbons of each surfactant) (19). In keeping with Rubing's advice, a C12 cationic surfactant, dodecyltrimethylammonium bromide (DTAB), will be used in this work. Previous spectroscopic studies on DTAB-SPFO systems suggest that mixed micellar solutions are formed while avoiding the formation of liquid crystals or precipitate (20,21).

In this work, the following formulation properties are considered: precipitation phase map, CMC, surface tension, and contact angle on Teflon®.

EXPERIMENTAL PROCEDURES

Materials. The cationic surfactant used in this study, dodecyl trimethyl ammonium bromide (DTAB, purchased from Sigma-Aldrich, 99% purity), was used without further purification. The anionic surfactants sodium octanoate (SOCT) and sodium perfluorooctanoate (SPFO) were prepared by neutralizing octanoic acid (purchased from Sigma-Aldrich, 98%) and pentadecafluoro octanoic acid (purchased from Sigma-Aldrich, Fluka brand, 95%) with sodium hydroxide (Sigma-Aldrich, 50% aqueous solution). The final pH of these solutions was adjusted to 8 ± 0.5. Sodium chloride was purchased from Sigma-Aldrich, 99.5%. Deionized water (18 Ω/cm) was used to prepare the surfactant solutions.

Methods. Precipitation phase diagrams. For each system, DTAB-SPFO and DTAB-SOCT, seven total surfactant concentration levels were evaluated: 1E–4 M, 2E–4 M, 5E–4 M, 1E–3 M, 2E–3 M, 5E–3 M, and 1E–2 M. For each surfactant concentration five anionic surfactant (SPFO or SOCT) to DTAB molar ratios were prepared (1:10, 1:3, 1:1, 3:1, and 10:1). Each solution contained 0.1M NaCl. These mixtures were frozen overnight and then thawed to 27 ± 1°C. The mixture was shaken once a day for one week before visually inspecting the samples for the presence of precipitate. In selected cases, a low-power red laser beam was shone to detect the presence of particles due to the scattering from dilute suspensions (Tindall effect).

Surface tension. Surface tensions were measured at 27 ± 1°C using the Wilhelmy plate method with a Krüss Tensiometer, model K12. Equilibrium surface tensions are reported throughout this work unless otherwise specified. The equilibrium surface tension value was confirmed when the surface tension did not change (within ±1 mJ/m^2) over a 15-minute period. Dynamic surface tension curves were obtained for selected systems.

Contact angle measurements. For selected systems, the contact angle on Teflon® was evaluated using a Ramé-Hert goniometer, model 100-00-115. Teflon® films were produced by carefully wrapping a glass slide with Teflon® tape (the tape was stretched over the surface to prevent wrinkles on the surface).

Evaluation of CMC and surface tension after CMC. CMCs were determined by plotting surface tension (γ) vs. natural logarithm of surfactant concentrations (ln C). A typical γ – ln C plot for a dilute solution of a surfactant or mixed surfactants has two parts: a linearly decreasing γ with increasing ln(C) (below the CMC) and a portion of constant γ with increasing ln(C) (above CMC). The critical micelle concentration (CMC) and surface tension after CMC were determined by intersecting the best fits of these two regions of the surface-tension-vs.-concentration curves (2).

RESULTS

Precipitation phase diagrams. No precipitate was observed for the mixture of DTAB-SOCT within the range of concentrations considered in this work. On the other hand, certain combinations of DTAB-SPFO did result in precipitate and coacervate phase formation. Figure 1 shows the precipitation phase map for the system DTAB-SPFO. As one could expect from the solubility product (Eq. 3), precipitate was found at high surfactant concentrations and equimolar DTAB and SPFO concentrations.

As it was discussed in the introduction, the precipitation phase boundaries can be predicted using the regular solution theory. Since the lowest equimolar concentration at which precipitate was observed for the system DTAB-SPFO was 1E–3 M, the solubility product Kp was estimated to be 1E–6 M^2. CMC_A° and CMC_B° were obtained from surface-tension data with systems containing 0.1M NaCl (shown later), and they were 2.0 E–3 M for SPFO and 3.0E–3 M for DTAB. It should be clarified that at 5E–3 M and 1E–2 M total concentration (and equimolar ratio) coacervate phases, instead of a precipitate, are obtained. Three precipitation phase boundary lines were produced assuming, values of 0, –1, and –1.25.

The phase boundary that corresponds to a β value of 0 includes, in the precipitate region, four experimental points where precipitate was not observed. On the other hand, β values of –1 and –1.25 are consistent with the experimental data, but it is not possible to discern which one is more accurate because of the resolution of the experimental grid.

It is worth highlighting that β values in the order of –1 to

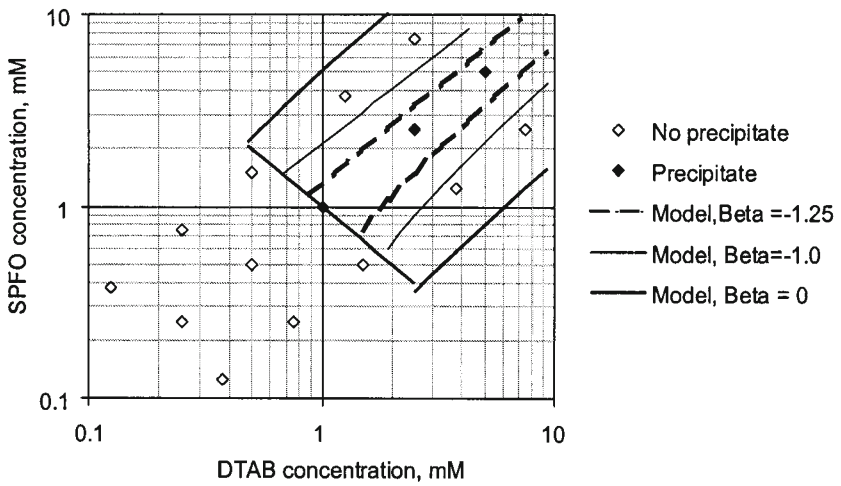

FIG. 1. Precipitation phase map for DTAB-SPFO at 27°C and in 0.1M NaCl solution.

–1.25 are typical of systems with "weak" attractive interactions (2). This is consistent with the findings of Yu and Zhao (22) that mixtures of anionic and cationic surfactants with asymmetric chain lengths do not produce as low surface tensions (i.e., less synergism) but at the same time do not produce turbid solutions (coacervates or precipitate).

Unfortunately, the literature does not present other precipitation phase diagrams for SPFO to which Figure 1 could be compared. Previous studies with SPFO-OCTAB and SPFO-hexylpyridinium bromide report that mixtures with total concentrations above 1 mM tend to produce coacervate turbid phases (5,22). With the exception of equimolar mixtures, the asymmetric combination of DTAB-SPFO was able to produce clear solutions even when the concentration was 10 mM.

It is necessary to keep in mind that at higher surfactant concentrations liquid crystals and coacervate phases may appear in addition to precipitate phases. The micelle-precipitate equilibrium model (Eq. 1–4) does not account for these other phase transitions.

DTAB-SPFO system (added electrolyte). DTAB-SPFO mixed-surfactant system (0.1M NaCl). In this case, a constant concentration of sodium chloride was maintained to be able to compare the CMC of the surfactant mixtures under similar ionic strength. The surface-tension-vs.-total-surfactant-concentration curves for the pure surfactants and mixtures containing 0%, 10%, 25%, 50%, 75%, 90%, and 100% of DTAB (SPFO to balance) are presented in Figure 2.

The data in Figure 2 shows that the surface tension after CMC is the same for all surfactant mixtures (~18 mJ/m^2), which is close to that of the pure SPFO and half the surface tension of pure DTAB. The surface tension of these systems is slightly higher than that obtained for mixtures of SPFO with OCTAB or hexylpyridinium bromide (15 mJ/m^2) (4,22). It is remarkable, however, that producing a mixture containing 10% of SPFO produces the same surface tension as an equimolar DTAB-SPFO mixture. In other words, it is possible to obtain low surface tensions while avoiding equimolar ratios that tend to induce precipitate formation.

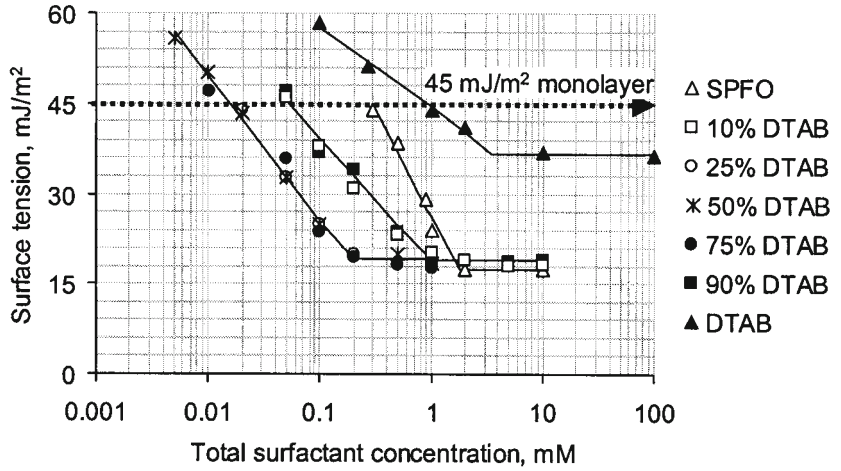

FIG. 2. Surface tension-concentration curve for DTAB-SPFO mixtures at 27°C, 0.1M NaCl.

Another interesting observation regarding the data in Figure 2 is that the adsorption curves (surface tension-concentration) for mixtures containing between 25% and 75% coincide with one another. This is also consistent with the results obtained for the SPFO-OCTAB system (4). This suggests that these surfactant films adsorbed at the air-water interface have similar composition.

One clear advantage of the DTAB-SPFO systems over the SPFO-OCTAB and SPFO-hexylpyiridinium bromide is that the CMC of the equimolar DTAB-SPFO mixture is one order of magnitude lower than these other systems. The lower CMC of the DTAB-SPFO system is a result of the low CMC of the cationic surfactant DTAB.

Another interesting feature of Figure 2 is that the slope of all mixed systems is approximately the same and intermediate between the pure surfactants. The slope of these curves can be converted into a surface-excess concentration (Γ) using the Gibb's adsorption equation (swamping electrolyte) (2):

$$\Gamma = \frac{-1}{RT}\left(\frac{d\gamma}{d\ln C}\right) \qquad [5]$$

where γ is the surface tension, C is the total surfactant concentration, R is the universal gas constant, and T is the absolute temperature of the system. From this equation the surface area per unit of surfactant molecule a can be obtained by the following:

$$a = \frac{10^{20}}{N_A \Gamma} \qquad [6]$$

where N_A is the Avogrado's number.

Table 1 summarizes the CMC, surface tension after CMC (γ_{CMC}), and surface area per surfactant molecule for the systems in Figure 2. For mixtures, this surface area per molecule is an average nominal value since, at this point, the surfactant composition at the interface is unknown. However, it is worth pointing out that the average surface area per molecule between pure SPFO and DTAB is 49 Å^2/molecule. This value is close to the average area per molecule for the mixed systems (Table 1), suggesting that the surface might be composed of an equimolar mixture of SPFO and DTAB.

From the application point of view, the data in Table 1 show that by producing a solution that contain 0.05mM SPFO and 0.15mM DTAB one obtains almost the same surface tension as using 2 mM of SPFO. Therefore, it is possible to reduce the required concentration of SPFO by 40 times and still achieve equivalent surface activity.

In addition to the surface properties discussed above, the surface tension data in Figure 2 can be used to evaluate the properties of the surfactant monolayer adsorbed at the air-water interface. In this work the monolayers that produce a surface tension of 45 mJ/m^2 are also studied. Note that the selection of surface tension is arbitrary [although typically 52 mJ/m^2 is used (2)]. Table 1 summarizes the total surfactant concentration required to produce a surface tension of 45 mJ/m^2 for each surfactant mixture (C45mJ/m^2). The data in Table 1 shows that mixed surfactant monolayers are formed at lower concentrations than the pure surfactant alone, which is consistent with the fact that mixed-surfactant micelles are also formed at lower total surfactant concentration. The difference between the micelle and monolayer data is that mixed-surfactant monolayers are formed at concentrations nearly two orders of magnitude lower than the pure surfactants, where as mixed-surfactant micelles are formed at concentrations nearly one order of magnitude lower. This observation suggests that the interaction between SPFO and DTAB is stronger when the molecules are adsorbed at the air-water interface than when the surfactants form a mixed micelle.

Dynamic surface tension of DTAB-SPFO mixed-surfactant system (0.1M NaCl). In order to evaluate the dynamics of mixed anionic-cationic surfactant adsorption, the surface tension of the solutions at a total concentration of 0.05 mM was tracked over 1.5 hr. Figure 3 summarizes the results of the dynamic surface tension studies.

The results shown in Figure 3 indicate that there is an "instantaneous" adsorption of the mixtures of SPFO and DTAB. This instantaneous adsorption in mixtures of anionic and cationic surfactants has been reported for mixtures of hydrocarbon-based surfactants (23). For mixtures of hexylpyridinium bromide and SPFO Zhang and Hao have reported adsorption times in the order of 10^{-2} seconds (22). These authors have proposed that the reason for this instantaneous adsorption is because the adsorbed layer at the air-water interface has a nearly net-zero charge. If there is no electrostatic repulsion to hinder the adsorption process, then molecular diffusion, and not adsorption, is the rate-limiting step. The earlier argument that the surface may be composed of an equimolar mixture of DTAB and SPFO is compatible with the mechanism of diffusion-controlled adsorption. This in-

TABLE 1
Surface adsorption properties for mixtures of SPFO-DTAB at 27°C, 0.1M NaCl.

% DTAB	CMC	Γ_{CMC}	Area per molecule, *a*	C45mJ/m^2
0	2 ± 1 mM	17 ± 1 mJ/m^2	27 ± 3 Å^2	0.3 ± 0.1 mM
10	1.0 ± 0.5 mM	19 ± 1 mJ/m^2	48 ± 4 Å^2	0.05 ± 0.02 mM
25	0.2 ± 0.1 mM	18 ± 1 mJ/m^2	46 ± 4 Å^2	0.02 ± 0.01 mM
50	0.2 ± 0.1 mM	18 ± 1 mJ/m^2	40 ± 3 Å^2	0.02 ± 0.01 mM
75	0.2 ± 0.1 mM	18 ± 1 mJ/m^2	50 ± 10 Å^2	0.011 ± 0.006 mM
90	1.0 ± 0.5 mM	19 ± 1 mJ/m^2	46 ± 4 Å^2	0.05 ± 0.02 mM
100	3 ± 1 mM	36 ± 1 mJ/m^2	71 ± 5 Å^2	1 ± 0.5 mM

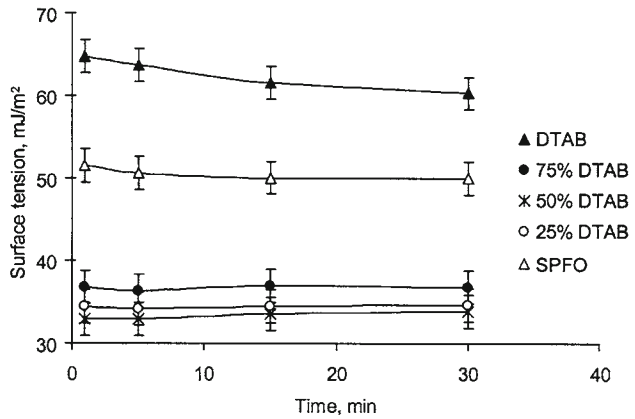

FIG. 3. Dynamic surface tension curves for DTAB-SPFO mixtures at 27°C, 0.1M NaCl (total surfactant concentration is 0.05 mM).

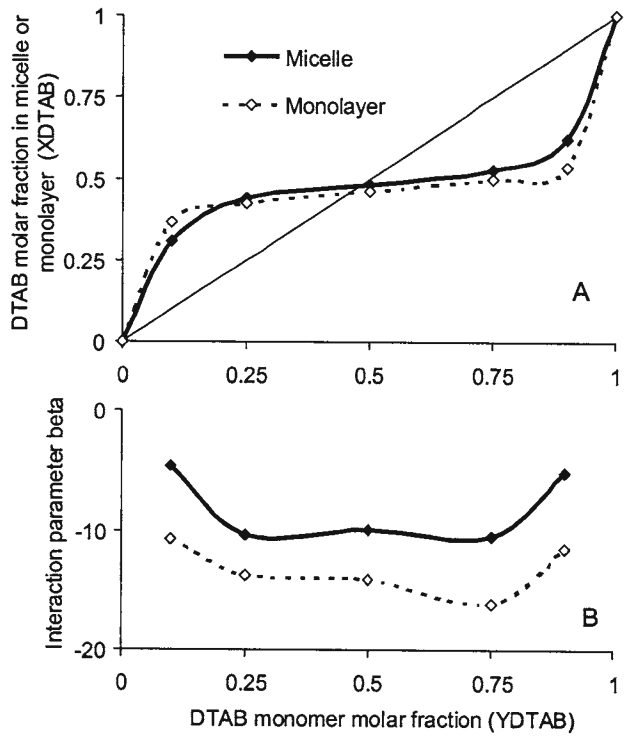

FIG. 4. Micelle composition (Part A) and beta interaction parameter (Part B) for DTAB-SPFO mixtures at 27°C, 0.1M NaCl.

stantaneous adsorption is desirable in the formulation of fire extinguishing foams, mineral separation, surface cleaning, agrochemical formulations, and others.

Regular solution theory applied to DTAB-SPFO mixtures (0.1M NaCl). The regular solution theory (Eqs. 1–2) was used to determine the interaction parameter β for the DTAB-SPFO mixed-surfactant system using the CMCs of the pure- and mixed-surfactants systems (Table 1). In addition, to find out the interaction parameter, this method helps in determining the compositions of the micelles at the CMC. Figure 4A shows the molar fraction of DTAB in micelles-X_{DTAB} (at the CMC) as a function of the molar fraction of DTAB as a monomer –(–Y_{DTAB}). Figure 4B shows the values of the interaction parameter , obtained for the different DTAB monomer molar compositions. In the case of Figure 4A, the calculations based on the regular solution theory suggest that the composition of the micelles at the CMC tend to approach an equimolar ratio (X_{DTAB} = 0.5). As the composition of the monomer approaches this equimolar ratio, the attractive interaction between SPFO and DTAB is comparable with that of mixed anionic-cationic hydrocarbon surfactants (β of –10), which insinuates the formation of ion pairs between these surfactants.

Similar to the micellar case, the regular solution theory can be used to calculate the composition and the interaction parameter , of the monolayer. To this end, the CMC terms in Equations 1 and 2 are replaced by the corresponding C45mJ/m^2 values in Table 1. The composition and interaction parameter , for the monolayer are presented in Figures 4A and 4B, respectively. In terms of composition, the monolayer, just like micelles, has an approximately equimolar composition of SPFO and DTAB. In fact, at a high DTAB-monomer molar fraction (YDTAB) the monolayer has a composition closer to equimolar than the micelle composition. The difference between micelles and monolayers become evident when one compares the interaction parameter β of Figure 4B. The larger negative value of β for the monolayer (compared to micelle) reflects the earlier observation regarding the relative value of the C45mJ/m^2 of the mixed surfactant systems with respect to the pure ones. Zhao *et al.* (24) have found in a DTAB-gemini anionic surfactant system that the interaction parameter of the monolayer is slightly larger and more negative than the corresponding micelle, ranging between –16 and –18 (close to the values presented in Figure 4B). The reason why the monolayer tends to produce an equimolar composition may be linked to the curvature of the monolayer and micelles. In micelles, the large curvature (small radius) helps offset the electrostatic repulsion between surfactants that have the same charge; thus, micelles have ways to accommodate a net positive or negative charge. For monolayers the curvature is zero, which makes it more difficult to accommodate net positive or negative charges, but if the surfactant adsorbs as an ion pair (as it was proposed based on the dynamic surface-tension studies), then electrostatic interactions do not oppose surfactant adsorption. Figure 5 illustrates the electrostatic interactions in SPFO, DTAB, and mixed-surfactant monolayers, showing the net attractive interactions in monolayers.

DTAB-SOCT system (added electrolyte): DTAB-SOCT mixed-surfactant system (0.1M NaCl). The purpose of this experiment was to evaluate the molecular interaction between cationic (DTAB) and anionic (SOCT) hydrocarbon-based surfactants, and compare their surface activity and interaction with the surface activity of a mixed fluorocarbon-hydrocarbon system (SPFO and DTAB) in the presence of 0.1M NaCl.

Figure 6 shows the surface tension-concentration curves for the pure surfactants and mixtures containing 25%, 50%, and 75% DTAB (SOCT to balance). Table 2 summarizes the main surface-activity parameters obtained from Figure 6.

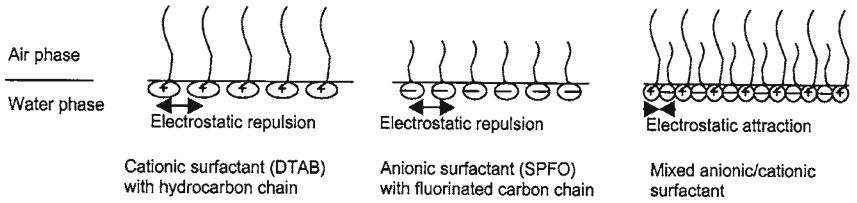

FIG. 5. Schematic of electrostatic interactions in monolayers of DTAB, SPFO, and mixed-surfactant systems.

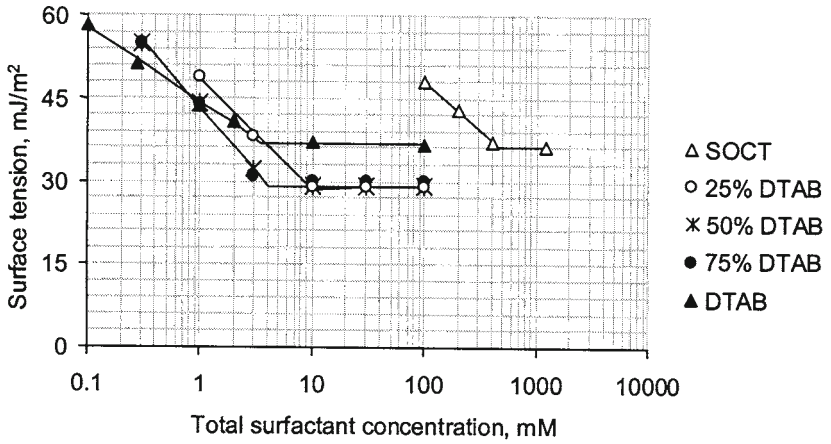

FIG. 6. Surface tension-concentration curve for DTAB-SOCT mixtures at 27°C, 0.1M NaCl.

One of the outstanding features of Figure 6 (compared to Figure 2) is that SOCT has a relatively large CMC (460 mM) compared to SPFO (2 mM). Also, the surface tension, after CMC, of SOCT is nearly twice that of SPFO. As expected, SPFO is a more surface-active molecule than SOCT. Fluorocarbon moieties are more hydrophobic than hydrocarbon moieties, which explains why SPFO molecules tend to associate in micelles at lower surfactant concentrations and adsorb at the air-water interface, leading to a reduction in equilibrium surface tension after CMC.

The CMCs of the DTAB-SOCT mixtures were higher than the CMC of DTAB due to the high CMC of SOCT. On the other hand, the surface tensions, after CMC, of the mixed systems were significantly lower than that of the pure surfactants. The surface tension, after CMC, for the DTAB-SOCT mixtures are the same (within the composition range of 25 to 75% of DTAB), which is consistent with the results obtained for the DTAB-SPFO system. From this last observation it is possible to hypothesize that the composition of DTAB-SOCT monolayers is the same regardless of the bulk composition (at least within the range of 25% to 75% DTAB). In the next section, the regular solution theory is used to estimate the composition of mixed micelles (at CMC) and mixed monolayers produced by mixtures of SOCT and DTAB.

Regular solution theory applied to DTAB-SOCT mixtures (0.1M NaCl). Using the CMC and C_{45} values obtained from Figure 6 and summarized in Table 2, the interaction parameter β for micelles and monolayers and their compositions was calculated using the mathematical procedure described above. Figure 7 summarizes these results.

Figure 7A shows the molar fraction of DTAB in micelles and monolayers versus the molar fraction of DTAB as a monomer in aqueous solution. The composition of micelles and monolayers is nearly constant between the range of 25% to 75% DTAB (as monomer), which is consistent with our earlier hypothesis that the composition of the monolayer

TABLE 2
Surface adsorption properties for mixtures of SOCT-DTAB at 27°C, 0.1M NaCl.

% DTAB	CMC	γ_{CMC}	Area per molecule, *a*	C45mJ/m^2
0	460 ± 40 mM	36 ± 1 mJ/m^2	52 ± 3 Å^2	150 ± 10 mM
25	10 ± 5 mM	29 ± 1 mJ/m^2	48 ± 4 Å^2	1.5 ± 0. 8 mM
50	5 ± 2 mM	29 ± 1 mJ/m^2	41 ± 3 Å^2	0.8 ± 0.3 mM
75	3 ± 2 mM	30 ± 1 mJ/m^2	40 ± 3 Å^2	0.8 ± 0.4 mM
100	3 ± 1 mM	36 ± 1 mJ/m^2	71 ± 5 Å^2	1.0 ± 0.5 mM

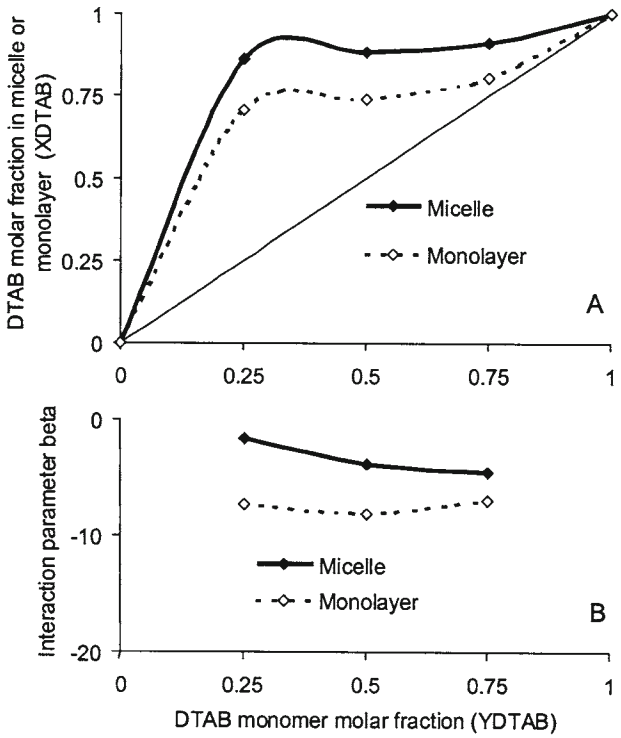

FIG. 7. Micelle composition (Part A) and beta interaction parameter (Part B) for DTAB-SOCT mixtures at 27°C, 0.1M NaCl.

(within the range of 25% to 75% DTAB) was almost constant. According to Figure 7A, the monolayer contains nearly 75% DTAB. The composition of the micelle at CMC was nearly 85%. These compositions are consistent with the fact that DTAB (CMC 3mM) is more surface-active than SOCT (CMC 460 mM). In the case of the DTAB-SPFO mixture, the nearly equal CMC of these surfactants contributed to the nearly equimolar composition of the micelles and monolayers.

When the interaction parameters presented in Figure 7B are compared with those of Figure 4B, one concludes that the interaction between DTAB-SPFO is stronger than that of DTAB-SOCT. This is a particularly surprising finding, since it is well known that in other mixed fluorocarbon-hydrocarbon surfactant systems (e.g., anionic-anionic, nonionic-nonionic) fluorocarbon moieties tend to segregate from hydrocarbon moieties (8,9,10). Since the ionic headgroups of both surfactants (SPFO and SOCT) are the same and the alkyl length is the same, one would hypothesize that the interaction between DTAB-SOCT would be larger (more negative) than between DTAB-SPFO. Part of the reason for this unexpected result is that the high CMC of SOCT reflects its high aqueous solubility; thus, SOCT has less driving force to produce micelles or mixed monolayers.

Similar to the DTAB-SPFO system, the monolayer interaction parameter for the DTAB-SOCT system is larger than that the micelle interaction parameter. However, the observed range for β of –8 to –10 for mixed DTAB-SOCT monolayers is almost half that observed by Zhao *et al.* for other hydrocarbon-hydrocarbon mixtures (24), which reflects the relatively mediocre interaction between SOCT and DTAB.

One last point that merits discussion is the surface area per molecule of DTAB-SPFO and DTAB-SOCT mixed-surfactant systems. The surface area per molecule of the SPFO is nearly half that of SOCT (compare Tables 1 and 2). This can be explained based on the greater tendency of SPFO to adsorb at the air-water interface (compared to SOCT) and escape the aqueous phase. Despite this significant different, the apparent surface area per molecule calculated for both surfactant mixtures (DTAB-SPFO, DABT-SOCT) are relatively close. The best way to compare these apparent or average surface areas is when the composition of the film is the same as the composition of the bulk solution. This occurs for 50% DTAB in DTAB-SPFO and 75% in DTAB-SOCT. In both cases the average surface area per molecule is minimum and equal to 40 $Å^2$/molecule. The fact that these minimum surface areas are the same suggests that the minimum surface area depends on the interaction and size of the ionic head groups (the same for both pairs). If one finds a combination with smaller surface area per molecule, it may be possible to ob-

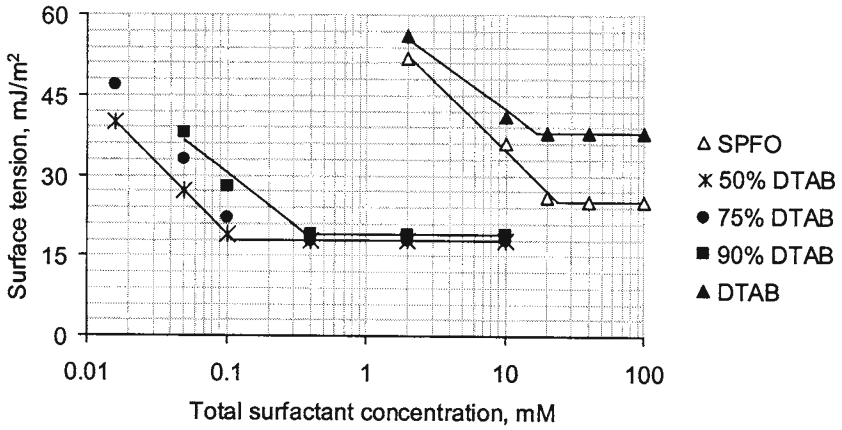

FIG. 8. Surface tension-concentration curve for DTAB-SPFO mixtures at 27°C, no added salt.

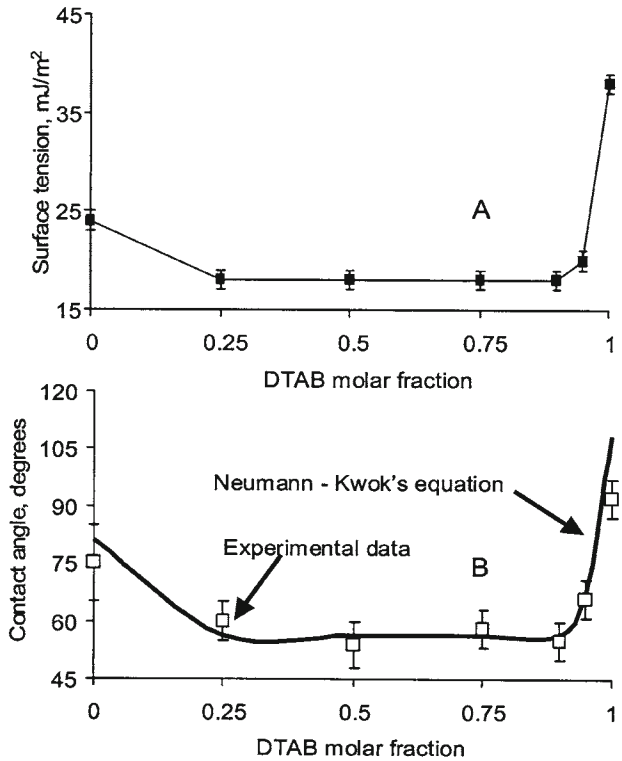

FIG. 9. Surface activity of DTAB-SPFO mixtures (no added salt) above their CMC. Part A: Surface tension. Part B: Dynamic contact angle on Teflon-coated glass slides.

tain lower surface tensions. In fact, mixtures of hexylpyridinium bromide (smaller surface area per molecule than DTAB) and SPFO can produce surface tensions as low as 15mJ/m^2 (22).

DTAB-SPFO system (no added electrolyte). The study of the DTAB-SPFO and DTAB-SOCT systems with added electrolyte allowed the molecular interactions between these anionic surfactants and DTAB to be studied, and established the role of fluorocarbon versus hydrocarbon-based surfactants. However, in some applications such as hard-surface cleaning, the addition of electrolyte is undesirable. To this end, we obtained the surface tension-concentration (adsorption) isotherms and the contact angle on Teflon®-coated surfaces for mixtures of SPFO and DTAB with no added electrolyte.

Surface tension studies. Figure 8 shows the adsorption isotherm for DTAB-SPFO without added electrolyte. This figure has two remarkable features. The first one is that the surface tension after CMC of the mixed surfactant system (18 mJ/m^2) is the same, independent of DTAB bulk composition (in the range of 50 to 90%), and is lower than that of the pure SPFO alone (24 mJ/m^2). The second feature is that the CMC of the mixed-surfactant system containing 50% DTAB (0.1 mM) is even lower than the CMC of the mixed DTAB-SPFO system containing 50% DTAB and 0.1M NaCl (0.2 mM) (Fig. 2). It is worth nothing that even lower CMCs (~0.01 mM) than those presented in Figure 8 have been obtained with equimolar mixtures of SPFO and hexyl pyridinium bromide without added electrolyte (22).

In practical terms, Figure 8 may have a significant impact on the way we formulate mixed anionic-cationic systems. Consider the following facts: One could formulate a solution containing 20 mM of pure SPFO and obtain a surface tension of 24 mJ/m^2, or instead, one could formulate a solution containing 0.05 mM of SPFO and 0.05 mM of DTAB and obtain a surface tension of 18 mJ/m^2, thus reducing the required SPFO concentration by 500 times.

The lack of added electrolyte magnifies the difference in surface activities between mixed anionic-cationic surfactants and the individual surfactants. Góralczyk has observed a similar behavior for mixed monolayers, where no added electrolyte systems have β-interaction parameters as large as –20; whereas systems containing 0.1M NaCl have β values of –12 (25). Typically in pure ionic surfactants, the addition of electrolyte reduces the CMC by reducing the thickness of the diffuse layer and the electrostatic repulsion between ionic headgroups that oppose micelle formation. As Góralczyk explains, in mixtures of anionic and cationic surfactants, electrostatic interactions favor the formation of micelles and monolayers; thus, the addition of electrolyte only hinders the formation of these self-assembled structures.

Finally, as noted above, the surface tension after CMC (Fig. 9A) is the same regardless of the bulk composition (in the range of 25% to 90% DTAB). Based on previous observations for systems formulated with 0.1MNaCl, the fact that the surface tension is low and independent of composition leads to the inference that the film adsorbed at the air-water interface may be composed of a nearly equimolar mixture of SPFO and DTAB.

Wetting on Teflon®-coated surfaces. Wetting reflects the ability of a liquid solution to spread over a solid surface. Thermodynamically, the process of wetting is driven by the difference in surface energies (or surface tensions) of the solid-gas interface ($\gamma_{s/g}$), the liquid-gas interface (γ_l), and the solid-liquid interface ($\gamma_{s/l}$). In general, if a solid has a low surface energy (small $\gamma_{s/g}$ value), such as the case of Teflon® surfaces, only liquids with low surface tensions will wet the surface. The critical surface tension (γ_s) is a more common measure of the surface energy of a solid and is defined as the maximum surface tension that a liquid should have in order to completely wet a solid surface. To estimate the contact angle of solutions with surface tensions larger than γ_s, it is possible to use the expression proposed by Kwok and Neumann (26):

$$\cos(\theta_{adv}) = -1 + 2\left(\sqrt{\frac{\gamma_s}{\gamma_l}}\right)\exp(-\beta_w(\gamma_l - \gamma_s)^2) \qquad [7]$$

where θ_{adv} is the advancing contact angle and β_W is a coefficient with a value of 0.0001247 (m/mN)^2. Figure 9B shows the dynamic contact angles (2–5 min contact time) of the same mixtures presented in Figure 9A on Teflon®-coated slides. In addition to the experimental data, Figure 9B also shows the contact angles predicted by Equation 7, using a critical surface tension (γ_s) of 14 mJ/m^2 and the surface tension data (γ_l) of Figure 9A.

The good match between the experimental data and the

prediction of Equation 7 reinforces the fact that the wetting properties of these mixtures are dominated by their surface tension. The value of critical surface tension of 14 mJ/m^2 is lower than the range reported in the literature for Teflon® (15–18 mJ/m^2), but this difference is relatively small considering that the coating surface was not completely smooth and that the contact angles measured were dynamic in nature (27).

Low-density polyethylene surfaces ($\gamma_s \sim 27$ mJ/m^2) were also evaluated, but since the DTAB-SPFO mixtures spread over these surfaces, the values of contact angles (zero) are not tabulated.

REFERENCES

1. Scheibel, J.J., The Evolution of Anionic Surfactant Technology to Meet the Requirements of the Laundry Detergent Industry, *J. Surfactant Detergents. 7(4):* 319–328 (2004).
2. Rosen M.J., *Surfactants and Interfacial Phenomena,* 2nd ed., John Wiley & Sons, New York, 1989.
3. Kissa, E., *Fluorinated Surfactants and Repellants,* Surfactant Science Series, Vol. 97, Marcel Dekker, Inc., New York, 2001.
4. Guo, W., E.K. Guzman, S.D. Heavin, Z. Li, B.M. Fung, and S.D. Christian, Mixed Surfactant Systems of Sodium Perfluorooctanoate with Nonionic, Zwitterionic, and Cationic Hydrocarbon Surfactants, *Langmuir 8(10):* 2368–2375 (1992).
5. Guo, W., B.M. Fung, S.D. Christian, and E.K. Guzman, Micellization in Mixed Fluorocarbon-hydrocarbon Surfactant Systems, *ACS Symposium Series 501 (Mixed Surfactant Syst.),* 1992, pp. 244–254.
6. Zhang, L. and G. Zhao, Dynamic Surface Tension of the Aqueous Solutions of Cationic-anionic Surfactant Mixtures, *J. Colloid Interface Sci. 127(2):* 353–361 (1989).
7. Hao, J., R. Lu, and H. Wang, NMR and ESR Studies on the Micro-environmental Properties of Perfluorooctanoate and Cetyltrimethylammonium Bromide Mixed Micelles Solutions, *J. Disp. Sci. Technol. 18(4):* 379–388 (1997).
8. Mukerjee, P. and K.J. Mysels, Anomalies of Partially Fluorinated Surfactant Micelles. *ACS Symposium Series, (Colloidal Dispersions Micellar Behav., Pap. Symp., 1974),* 1975, pp. 239–252.
9. Mysels, K.J., Critical Demicellization Concentration? *J. Colloid Interface Sci. 66(2):* 331–334 (1978).
10. Shinoda, K. and T. Nomura, Miscibility of Fluorocarbon and Hydrocarbon Surfactants in Micelles and Liquid Mixtures: Basic Studies of Oil Repellent and Fire Extinguishing Agents, *J. Phys. Chem. 84(4):* 365–369 (1980).
11. Jung, H.-T., S.Y. Lee, E.W. Kaler, B. Coldren, and J.A. Zasadzinski, Gaussian Curvature and the Equilibrium among Bilayer Cylinders, Spheres, and Discs, *Proceedings of the National Academy of Sciences, 99(24),* 2002, pp. 15318–15322.
12. Doan, T., E. Acosta, J.F. Scamehorn, and D.A. Sabatini, Formulating Middle-Phase Microemulsions Using Mixed Anionic and Cationic Surfactant Systems, *J. Surfactant Detergents 6(3):* 215–224 (2003).
13. Rubingh, D.N., Mixed Micelle Solution, in *Solution Chemistry of Surfactants,* edited by K.L. Mittal, Vol. 1, Plenum, New York, 1979, pp. 337–353.
14. Scamehorn, J.F. and J. H. Harwell, Precipitation of Surfactant Mixtures, in *Mixed Surfactant Systems,* edited by K. Ogino and M. Abe, Surfactant Science Series, Vol. 46, Marcel Dekker, New York, 1993, pp. 283–300.
15. Stellner, K.L., J.C. Amante, J.F. Scamehorn, and J.H. Harwell, Precipitation Phenomena in Mixtures of Anionic and Cationic Surfactants in Aqueous Solutions, *J. Colloid Interface Sci. 123:*186 (1987).
16. Amante, J.C., J.F. Scamehorn, and J.H. Harwell, Precipitation of Mixtures of Anionic and Cationic Surfactants, II: Effect of Surfactant Structure, Temperature and pH, *J. Colloid Interface Sci. 144:* 243 (1991).
17. Jokela P., B. Joensson, and H. Wennerstroem, Phase Equilibria in Systems Containing both an Anionic and a Cationic Amphiphile: A Thermodynamic Model Calculation, *Prog. Colloid Polym. Sci. 70:* 17 (1985).
18. Yakov, L. and E. Kaler, Formation of Surfactant and Polyelectrolyte Gel Particles in Aqueous Solutions, *Colloid Surfaces, A 250(1–3):* 179–187 (2004).
19. Rubingh, D.N., Surface Active Cationic Compounds in Detergency, in *Cationic Surfactants Physical Chemistry,* edited by D.N. Rubingh and P. M. Holland, Surfactant Science Series, Vol. 37, Marcel Dekker, Inc., New York, 1991.
20. Jing-Cheng, H., W. Han-Qing, L. Wei-Min, and L. Gan-Zuo, Studies on the Microenvironment Properties of the Mixed Micelles of SPFO-DTAB by NMR and ESR, *Huaxue Xuebao 55(4):* 322–327 (1997).
21. Huijun, D., C. Shaomo, W. Lu, and Z. Guoxi, Interface Chemical Properties of the Mixed Aqueous Solution of Sodium Perfluorooctanoate and Alkyltrimethylammonium Bromide, *Huaxue Xuebao 4(6):* 629–635 (1988).
22. Yu, Z., and G. Zhao, The Physicochemical Properties of Aqueous Mixtures of Cationic-Anionic Surfactants, I: The Effect of Chain Length Symmetry, *J. Colloid Interface Sci. 130:* 2 (1989).
23. Smith, C., P. Duane, E.J. Lin, P. Zhang, and R.K. Pinschmidt, U.S. Patent No. 7097705 (2006).
24. Zhao, J.X., X.F. Yang, R. Jiang, Y.H. Ma, and J.J. Cao, Adsorption Layer Structure Formation at the Air/Water Interface in Aqueous Mixtures of an Anionic Carboxylate Gemini and a Cationic Surfactant, *Colloid Surf. A 275:* 142–147 (2006).
25. Góralczyk, D., Application of the Regular Solution Model to Anionic-Cationic Adsorption Films, *Colloid Surf. B 59:* 361–370 (1991).
26. Kwok, D.Y. and A.W. Neumann, Contact Angle Measurement and Contact Angle Interpretation, *Adv. Colloid Interface Sci. 81(3):* 167–249 (1999).
27. Neumann, A.W. and J.K. Spelt, *Applied Surface Thermodynamics,* Marcel Dekker, Inc., New York, 1996.

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