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Two-Site Adsolubilization Model of Incorporation of Fluoromonomers into Fluorosurfactants Formed on Cotton Fabric

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ABSTRACT: The adsorption of surfactants and adsolubilization of organic compounds on knit cotton fabric are fundamentally important in admicellar polymerization to impart characteristics like water repellency, stain resistance, and flame retardancy. The main objective of this research is to study adsorption and adsolubilization of fluorsurfactants and fluoromonomers used to obtain water repellency characteristics. Adsorption of nonionic (fluoroaliphatic amine oxide) and cationic (fluoroaliphatic quaternary ammonium surfactant) fluorsurfactants at the interface of cotton is investigated with and without fluoroacrylate monomers. A two-site adsolubilization model was used to predict the aggregation number of fluorosurfactant.
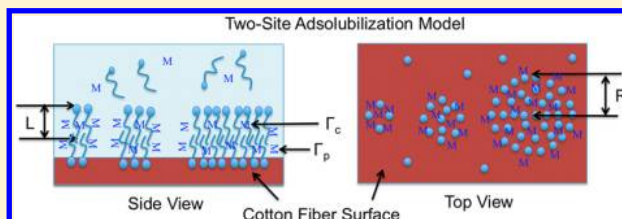
INTRODUCTION

A great deal of work has been done on surfactant adsorption and adsolubilization at solid/liquid interfaces over the past few decades. Adsorbed aggregates (admicelles and hemimicelles) are formed on solid surfaces above the critical admicelle concentration (CAC) and lower than the critical micelle concentration (CMC). Factors like electrostatic attraction, hydrogen bonding, and lateral interactions between adsorbed species help to determine conditions leading to admicelles in a particular combination of surfactant, solvent, and substrate.[1]

Whether continuous or discrete, admicelles act to concentrate species at the interface as they incorporate sparingly soluble organic compounds that are poorly adsorbed or not adsorbed at all in the absence of surfactant. While surfactant adsorption potentiates adsolubilization, the presence of adsolubilizate can reciprocally influence adsorption of surfactant due to the nature of the interactions of the organic species with the solvent and amphiphile. Fundamental knowledge on adsorption and adsolubilization has aided the development of applications. These include surfactant-based separation processes,[2,3] isolation of pharmaceuticals,[4,5] formation of polymeric thin films,[6−12] material synthesis for cosmetics and health care,[13] wastewater treatment,[14−17] and reactions by admicellar catalysis.[18] In particular, adsolubilization of monomer enabled admicellar polymerization over solid substrates like titanium dioxide,[19] polyester,[20] collagen fibers,[21] cotton,[8,9] alumina, and silica.[22,23]

The range of utility reflects how adsolubilization can occur over many substrates with suitable choice of surfactant and conditions. Research has been carried out on adsolubilization and the effect of solution pH, surfactant concentration, and type of hydrocarbon surfactant for solid surfaces like alumina, precipitated silica, and cellulose fiber by utilizing different hydrocarbon compounds.[24−27] The concept of adsolubilization phenomena of organic compounds on different solid surfaces

with single and mixed surfactant systems has been reviewed by Esumi.[28]

In general, adsolubilization increases with the extent of the admicellar phase. Li and Wang, for example, found that adsolubilization of dihydroxybenzene into cetyltrimethylammonium bromide (CTAB) over silica increases with surfactant concentration and saturates at CMC of CTAB.[29] The sites available for incorporation of molecular species are greater as surfactant coverage approaches plateau adsorption, while the nature of these sites can change according to the two-site adsolubilization model. The two-site adsolubilization model derives from the concept of patchwise adsorption which incorporates counterion concentrations, surfactant surface aggregation, surface heterogeneities, and hydrophobic effect to estimate surface adsorption values.[30] With patchwise adsorption, species can partition within adsorbed surfactant aggregates and at the outer perimeter of aggregates, as illustrated in Figure 1. Comparison of findings for alcohols and alkanes provided insight for the two-site adsolubilization model. At low coverages, the ratio of aliphatic alcohols to surfactant is high and decreases to a constant value for plateau adsorption. Alkanes, however, partition only into the interior with similar ratio over the full isotherm.[31] Interestingly, See has reported observation of a two-dimensional level transition with adsolubilization of styrene in cetyltrimethylammonium bromide (CTAB) aggregates.[32] These observations were important to the confirmation of the two-site model.[30] Other work by Behrends suggests that location within the admicelle is different still for aromatic compounds, the study of which led to a three-site adsolubilization model.[33]

Lee et al. applied the two-site adsolubilization model to the adsorption of sodium dodecyl sulfate and adsolubilization of
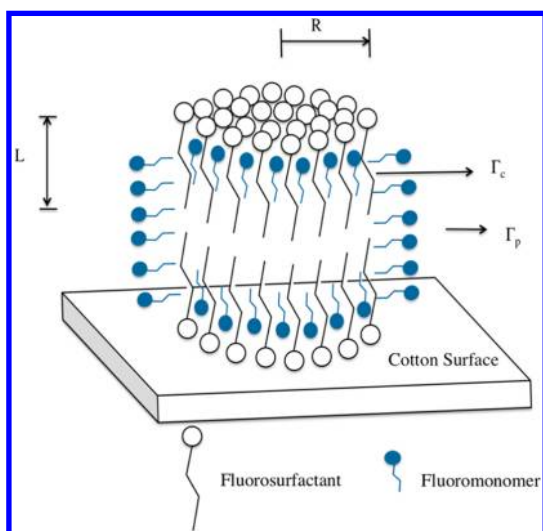
Figure 1. Two-site adsolubilization model.

different alcohols and alkanes on alumina.[31] His results yielded estimates of the admicellar aggregation numbers for that system. Aggregation numbers for sodium dodecyl sulfate (SDS) ranged from 60 molecules/aggregate at one hundredth of bilayer coverage (0.06 molecules/nm²) to 25000 molecules/aggregate at one-half bilayer coverage (3.3 molecules/nm²). In the region of the isotherm near the onset of cooperative adsorption, aggregation numbers on the order of 60 were found in good agreement with estimates obtained by fluorescence quenching.[34]

Little work has been done on adsolubilization with fluorocarbon systems. Lai et al. studied the adsolubilization of fluorocarbon alcohols in perfluoroheptanoate surfactant admicelles on alumina.[35] He determined adsolubilization constants on the order of 10 to 20 to 150 for 2,2,2-trifluoroethanol (FEtOH), 2,2,3,3,3-pentafluoropropanol-(FPrOH), and 2,2,3,3,4,4,4-heptafluorobutanol(FBtOH), a trend opposite to that for similar hydrocarbon systems. Compared to adsorption of hydrocarbon surfactant and adsolubilization of hydrogen compound interactions, adsorption of fluorosurfactants and fluorocompounds has stronger hydrogen bonding and can have large partition coefficients. As such, these systems merit further research.

The objective of this paper is to study adsorption of zwitterionic and cationic fluorosurfactants and the adsolubilization of fluoromethacrylates on a cotton surface. The two-site model was used to estimate the aggregation numbers and partition coefficients. This study will advance understanding of the amount of fluoromonomers and fluorosurfactants adsolubilized to form fluoropolymer on surface of cotton to impart oil/water repellent characteristics.[36]

■ THEORY

Figure 1 shows an illustration of the two-site adsolubilization model for fluoromonomer adsolublized into fluorosurfactant admicelles. One site for adsolubilization is in the palisade layer of the admicelle core between headgroups of fluorosurfactant molecules represented as Γ_c. The other site for adsolubilizates with a hydrophobic moiety is on the hydrophobic perimeter of cylinder-shaped admicelles represented as Γ_p. The total adsolubilized amount of alcohol (Γ_a) can be expressed as

$$\Gamma_a = \Gamma_c + \Gamma_p \tag{1}$$

The partition coefficient (K) of fluoromonomer between admicellar and bulk phases is defined as follows:

$$K = \frac{X_a}{C_a} \tag{2}$$

$$X_a = \frac{\Gamma_a}{\Gamma_s} \tag{3}$$

where X_a is ratio of adsorbed monomer (Γ_a) per adsorbed amount of fluorosurfactant (Γ_s) and C_a is equilibrium concentration of fluoromonomer in supernatant. We assume there are no micelles present in the supernatant at equilibrium.

At very high surface coverage, close to bilayer formation, the contribution of Γ_p to two-site adsolubilization becomes much less significant with a decrease in ratio of perimeter area sites to palisade layer sites. In this case, when fluorosurfactant adsorption reaches a complete bilayer ($\Gamma_a \cong \Gamma_c$), experimentally measured partition coefficient for fluoromonomer K_b approximates as

$$K_b = \frac{\Gamma_c}{\Gamma_s C_a} \tag{4}$$

In order to express the adsolubilized amount of fluoromonomer on perimeter of fluorosurfactant aggregates, the lateral surface area, A_l, of a right circular cylinder of radius R and height $2L$, as shown in Figure 1, can be calculated from

$$A_l = 4\pi R L \tag{5}$$

where L is the chain length of a fluorosurfactant. Since the two bases of right circular cylinder are composed of headgroups of fluorosurfactant aggregates, the mathematical expression can be stated in terms of cross-sectional area per fluorosurfactant molecule (A_s) and the average aggregation number (N_{avg}) are calculated from

$$2\pi R^2 = N_{avg} A_s \tag{6}$$

From an assumption that the hydrophobic lateral surface area (A_l) resembles an oil/water interface to the fluoromonomer molecules, one can obtain the value of adsorbed molecules for a fluoromonomer monolayer, A_l/A_a, in which A_a is cross-sectional area per fluoromonomer molecule. After multiplying this value by the number of cylinder-shaped fluorosurfactant aggregates (Γ_s/N_{avg}), adsolubilized amounts of the fluoromonomer on the hydrophobic perimeter of cylinder-shaped admicelles can be estimated as

$$\Gamma_p = \frac{A_l \times \Gamma_s}{A_a \times N_{avg}} \tag{7}$$

The combination of equation from 1 and 3−7 yields an average aggregation number in terms of known quantities as

$$N_{avg} = \frac{8\pi L^2 A_s}{A_a^2}(X_a - K_b C_a)^{-2} \tag{8}$$

Numerical values of parameters were listed in Table 2.

■ MATERIALS

Interlock knit cotton fabric (0.31 m²/g) was purchased from Alamac American Knits. The fabric obtained was scoured prior to use. Fabric was washed repeatedly until it was free from any
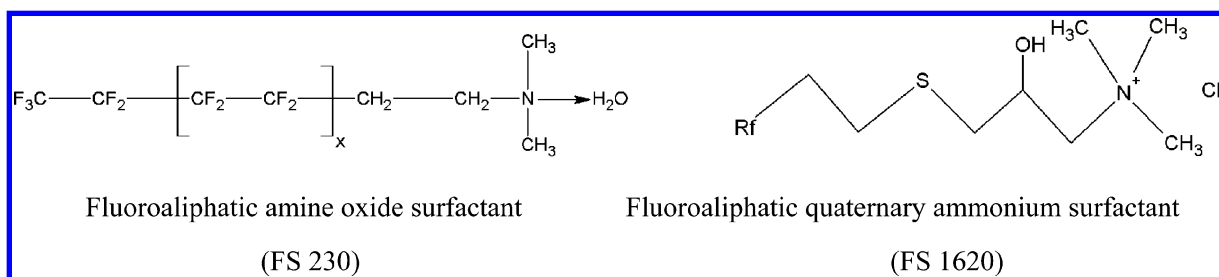
Figure 2a. Structures of commercial fluorosurfactants FS230 and FS1620.
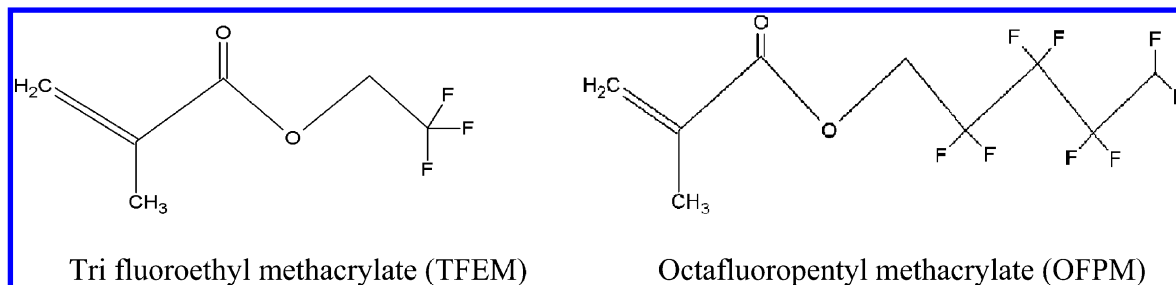

Figure 2b. Structure of fluoromonomers TFEM and OFPM.

remaining surfactant. Zwitterionic fluoroaliphatic amine oxide surfactant (FS230: 30% active matter) and cationic fluoroaliphatic quaternary ammonium fluorosurfactant (FS1620: 20% active matter) were obtained from Mason Chemicals (Figure 2a). Fluoromonomers used were octafluoropentyl methacrylate (OFPM) and trifluoroethyl methacrylate (TFEM) purchased from Synquest Laboratories Inc. (Figure 2b). Chemicals were used as obtained without further purification.

■ EXPERIMENTAL SECTION

Cotton swatches (2.0 g) were placed in 20 mL vials. Fluorosurfactant solutions of various concentrations with a specific concentration of fluoromonomer were added to vials. Solution pH was maintained at 7 without any headspace left in vials. Vials were sealed with aluminum foil and capped with Teflon-lined septa held in place with polypropylene caps. Samples were equilibrated at 60 °C for 2 h in a shaker bath and kept at room temperature for equilibration for 14 h for adsorption and adsolubilization to take place. A small amount of aliquot from vials was filtered with 0.45 μm size filters for analysis for HPLC. Adsorption and adsolubilization measurements were determined from concentration changes by using a C18 surfactant column (RESTEK) (dimensions of 250 × 4.6 mm) with an evaporative light-scattering detector for surfactants FS230 and FS1620 and a UV−vis detector for fluoromonomers (245 nm).

Mobile phases used for analysis were methanol and water in ratios of 70:30 for FS230 and 80:20 for FS1620, while fluoromonomers OFPM and TFEM were assayed with mobile phase ratio of 70% methanol and 30% water. HPLC analysis was carried out for fluorosurfactants dissolved in HPLC-grade water and for fluoromonomers dissolved in HPLC-grade isopropanol to obtain retention times and to check for impurities. The peaks obtained by analysis of the fluoromonomers and fluorosurfactants were single peaks of high intensity. Calibration curves were obtained for fluorosurfactants and fluoromonomers followed by measurements to obtain adsorption isotherms and adsolubilization results. Experiments were repeated for different concentrations ranging from 0.01 to 100 mM for surfactants and 5 mM for the concentration of monomers.

■ RESULTS AND DISCUSSION

Adsorption Isotherms of Fluorosurfactants. Adsorption isotherms of the fluorosurfactants (FS230 and FS1620) alone and in the presence of fluoromonomers (OFPM and TFEM)
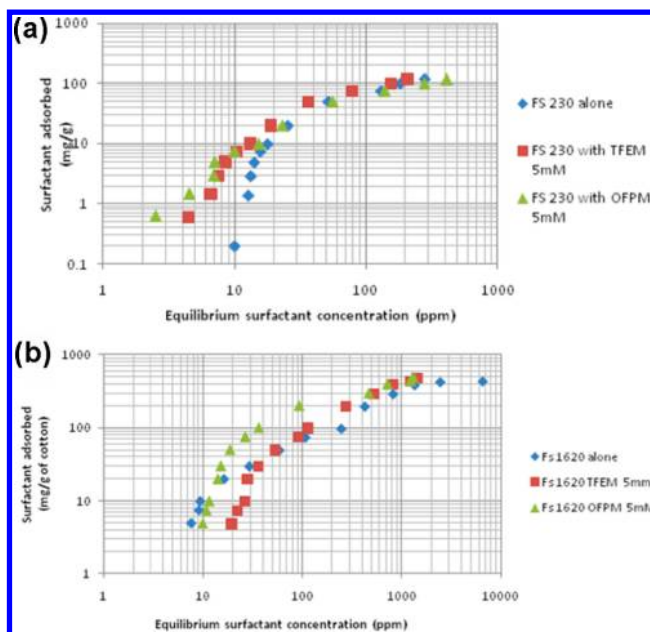

Figure 3. Adsorption isotherms of surfactants alone and in the presence of monomers.

are plotted in Figure 3. Adsorption rises rapidly at lower concentrations with formation of surface aggregates. At the solid−liquid interface, available sites for adsorption on the cotton surface decrease as the supernatant concentration increases. For both surfactants, as surfactant concentration increases the surface becomes saturated, leading to onset of micellization. Overall, the adsorption isotherms obtained for FS1620 and FS230 are comparable to isotherms obtained for hydrocarbon surfactants and other fluorocarbon surfactants.[3,35,37−39] However, FS230 and FS1620 will have lower CACs and CMCs than corresponding hydrocarbon surfactants because the fluorocarbon chain is more hydrophobic.

In Figure 3b, at around a concentration of 200 ppm, a stepwise coverage was observed for FS1620 alone. Inflection points have been widely observed in surfactant isotherms on
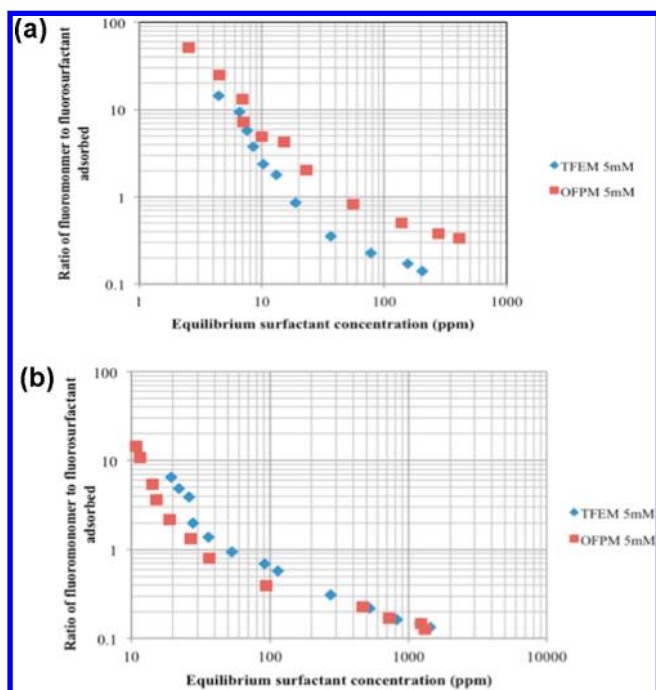
Figure 4. Ratio of adsolubilized fluoromonomer to adsorbed fluorosurfactant.
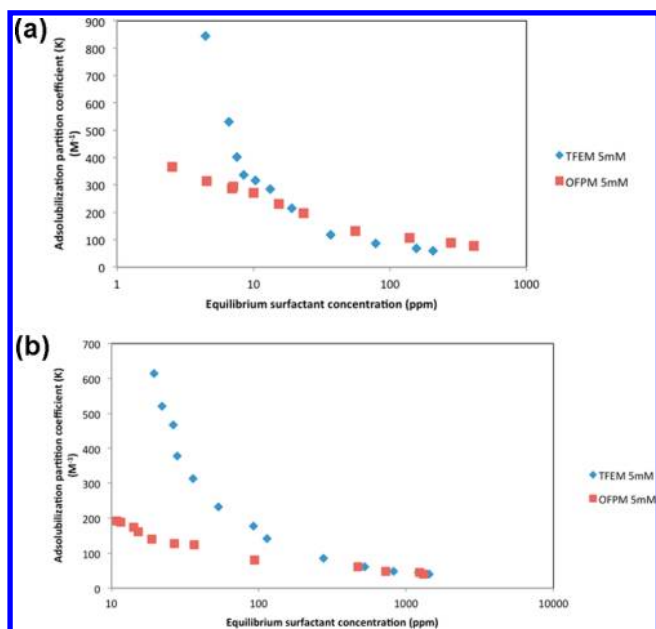

Figure 5. Adsolubilization partition coefficients for (a) FS230 and (b) FS1620.

mineral substrates. These often can be attributed to surface heterogeneities, such as the adsorption of cationic surfactants on the edges or basal surfaces of kaolinite.[40] Cotton cellulose does have a high degree of crystallinity with amorphous regions[41] so that surface heterogeneities cannot be ruled out. However, the transition can be explained by another mechanism. Hydroxyl and thioether moieties in FS1620 may hydrogen bond to the cotton substrate at low coverages with a shift in orientation occurring at the inflection point to favor intersurfactant hydrogen bonding. Reorientation will enable greater lateral interactions of the hydrophobe in addition to intermolecular hydrogen bonding to facilitate the adsorption of

additional surfactant. The absence of the inflection point in the presence of the monomer adsolubilizates results from their ability to hydrogen bond in the core.

The presence of a monomer affects the adsorption isotherms of the two surfactants differently. Results for FS230 are alike with TFEM and OFPM, while the isotherms for FS1620 are distinct for the two monomers. In Figure 3a, at lower supernatant concentrations, both fluoromonomers significantly increase adsorption of F230. Since the molecular structures of OFPM and TFEM (Figure 2b) differ in the fluoroalcohol component of the methacrylate ester, the similar effect of enhanced adsorption at low surfactant concentration must be due to the carboxylate portion of the adsolubilizate. Given the high ratio of monomer to surfactant under these conditions (Figure 4a), we attribute the shift in the isotherm to a reduction in the rearrangement of water molecules for surfactant in solution versus surfactant in admicelles. For the latter, the hydrophobe is shielded by monomer at the periphery of the admicelles. As coverage increases, the FS230 isotherms merge.

In contrast, the effect of monomer on the adsorption of FS1620 is different for OFPM and TFEM (Figure 3b). Data indicate the presence of OFPM increases surfactant adsorption while TFEM decreases coverage. Structural comparison suggests the fluorocarbon moieties account for the behaviors observed. We suggest that greater lateral interaction of the longer fluorocarbon moiety facilitated by the much poorer solubility of OFPM causes enhanced adsorption. It is less clear what causes the reduced adsorption of FS1620 in the presence of TFEM, but it may be due to greater solubility of this surfactant in water with the presence of a rather soluble monomer.

For all cases, the fluoromonomer adsorption has negligible effect on adsorption near the CMC where adsorption of fluorosurfactants levels off. FS230 and FS1620 exhibit a peak adsorption of 100 mg/g of cotton at CMC of 300 ppm and 300 mg/g of cotton at a CMC of 3400 ppm, respectively. The CMC values of fluorosurfactants obtained from adsorption analysis were in reasonable agreement with those by surface tension analysis, as CMC of FS230 is 280 ppm and FS1620 is 3600 ppm, respectively.[42] CMC of the zwitterionic surfactant is less than that of the cationic surfactant because charge repulsion between head groups is less for the zwitterionic species. The lower adsorption of FS230 compared to cationic FS1620 can be explained by charge attraction since point of zero change (PZC) for cotton is 3[43] and pH in the reactor vial was maintained at 7.

It should be noted that, absent of surfactant, OFPM and TFEM adsorption was negligible. Monomer solubility influenced the behavior in the systems as it does in micellization, playing an important role in either increasing or decreasing the CMC. As chain length of fluorocarbon compounds increase, solubility of monomers in water decrease, thus facilitating partitioning in the micelles.[35] At higher concentrations, fluoromonomers can act as cosolvents and reduce hydrophobic attractions and increase the CMC.[44]

Adsolubilization of Fluoromonomers. The concentration of fluoromonomers TFEM and OFPM on the surface of cotton required the presence of fluorosurfactant, and observations confirm that the level of adsolubilization depends on extent of adsorption of the fluorosurfactant. Determination of the relative amounts of surfactant and monomer at the substrate surface for different system compositions helps to enhance understanding of the nature of the admicelle with

Table 1. Comparison of Adsolubilization Partition Coefficient with Fluorocarbon and Hydrocarbon Systems

surfactant	monomer	substrate	adsolubilization partition coefficient (M^{-1})	ref
sodium dodecyl sulfate (SDS)	butanol	alumina	600	45
	pentanol		150	
	hexanol		55	
	heptanol		16	
sodium dodecyl sulfate (SDS)	pyrrole	alumina	19.9	50
sodium dodecyl sulfate (SDS)	styrene	alumina	300	46
cetyltrimethylammonium bromide (CTAB)	styrene	precipitated silica	250	47
Triton X-100	styrene	silica	220	48
hexadecyltrimethylammonium bromide (C_{16}TAB)	naphthalene	precipitated silica	3000	51
cetylpyridinium chloride (CPyCl)	2-naphthol	silica	870	52
sodium perfluoroheptanoate	trifluoroethanol	alumina	15	35
	pentafluoropropanol		28	
	heptafluorobutanol		150	
lithium perfluorooctanesulfonate (LiFOS)	hexanol	alumina	402	26
	heptafluorobutanol		270	
lithium dodecyl sulfate (LiDS)	hexanol	alumina	314	26
	heptafluorobutanol		210	
fluoroaliphatic amine oxide surfactant (FS 230)	OFPM	cotton	76	
	TFEM		58	
fluoroaliphatic quaternary ammonium surfactant (FS 1620)	OFPM	cotton	66	
	TFEM		72	

Table 2. Numerical Values Used for Calculating Aggregation Number in Two-Site Adsolubilization Model

	FS230		FS1620	
category	TFEM	OFPM	TFEM	OFPM
L^a (nm)	1.5	1.5	2.5	2.5
$A_S{}^b$ (nm^2)	0.47	0.47	0.45	0.45
$A_A{}^c$ (nm^2)	0.263	0.263	0.263	0.263
$K_{APC}{}^d$ (M^{-1})	58	76	76	66

[a]Theoretical length of a fully extended fluorocarbon tail of surfactant. [b]Adsorption density of a fluorocarbon surfactant at the air/water interface. [c]Adsorption density of a fluoromonomer monolayer at the oil/water interface. [d]Estimated from an experimentally measured partition coefficient at a bilayer coverage.

adsolubilization and provides evidence for the two-site conceptualization. The ratio of fluoromonomer adsolubilized to fluorosurfactant adsorbed decreases with increasing supernatant concentration of surfactant before beginning to level off at or near the CMC (Figure 4). This reflects a higher proportion of perimeter sites available for many small admicelles at low coverage while core sites dominate as coverage approaches saturation.

Similar overall behavior was observed for both zwitterionic and cationic surfactant systems. The effect of monomer chains on the ratio, however, was different for the two surfactants. In the case of zwitterionic (FS230) surfactant, the chain length dependence of monomer had a distinct effect on the ratio of monomer to surfactant at higher supernatant concentrations of FS230. Higher ratios were found as the ester alcohol chain length changed from C3 monomer (TFEM) to C8 monomer (OFPM) (Figure 4a). This finding can be explained by much poorer water solubility of OFPM compared to TFEM. While lateral interactions between fluorocarbon moieties will be superior for OFPM, they cannot explain the results for FS 1620, where similar ratios are seen for the two monomers (Figure 4b). We believe the hydroxyl group in this surfactant causes
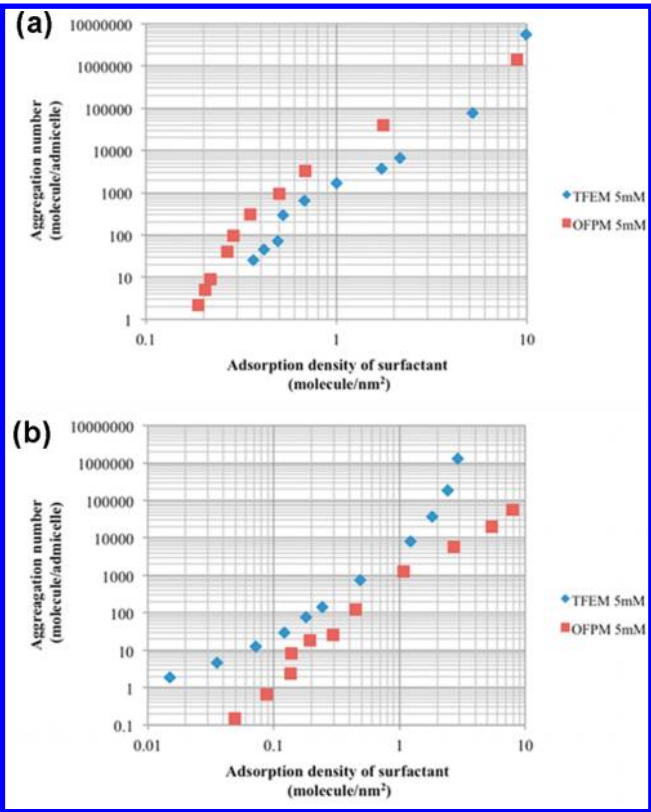

Figure 6. Aggregation number for fluorosurfactants in the presence of fluoromonomers.

more water molecules to be present in the admicelles of 1620, thereby facilitating adsolubilization of TFEM.

The decreasing trend in the ratio of monomer to surfactant generally follows observations by Yeskie[45] for hydrocarbon systems and reflects the transition from perimeter sites to palisade sites. The trend is characteristic of two-site adsolubilization and was observed also for fluorocarbon systems

by Lai who studied fluoroalcohol adsolubilization in perfluoroheptanoate surfactant on the alumina surface.[35] In regions of high surface coverage, the ratio of fluoromonomer to fluorosurfactant decreases due to balance between increase of fluorosurfactant adsorption on the surface and available space for fluoromonomer adsolubilization within the core of admicelles.

The partition coefficient for adsolubilization decreases rapidly for TFEM and more gradually for OFPM before becoming constant with increasing equilibrium fluorosurfactant concentration (Figure 5). As surfactant concentration increases, the partition coefficient changes more rapidly for TFEM monomer than for OFPM monomer. This is true for both the zwitterionic and cationic fluorosurfactants. The greater water solubility of TFEM makes it better-suited to occupy peripheral sites, which exist in greater proportion at less coverage. In contrast hydrophobic OFPM exhibits little tendency to occupy sites outside of the core. As peripheral sites disappear with increasing surfactant concentration, the partition coefficient becomes similar for all systems tested with values on the order of 100 M^{-1}.

These results compare favorably with Lai's observations at 0.01 M feed concentrations of fluoroalcohol adsolubilized in admicelles of perfluoroheptanoate surfactant,[35] in which partition coefficients were reported in the range from 15 to 150 M^{-1} with different fluoroalcohols (Table 1). Lai found that the adsolubilization constant increased with chain length in contrast to the trend for partition coefficients obtained by Yeskie for aliphatic alcohols in sodium dodecyl sulfate.[45] The values for adsolubilization of styrene exhibit a slight dependence on the type of surfactant decreases from anionic to cationic to nonionic, regardless of the substrate used (Table 1).[46−48] While it is difficult to draw firm conclusions from these data, fluorocarbon surfactant and fluorocarbon adsolubilizates systems generally have lower partitioning coefficients than do hydrocarbon surfactant and hydrocarbon species because fluorocarbon chains are less flexible and the fluorocarbon system is more hydrophobic.[26] This basis can explain Esumi's comparison of the adsolubilization of hexanol and heptafluorobutanol in fluorosurfactants where the hydrophobicities of the alcohols are expected to be similar and yet the adsolubilization constant is greater for hexanol. The admicelle/aqueous partition coefficients for the solutes are governed by molecular packing density in the admicelle, solute-surfactant headgroup interaction, and the aqueous solubility of the solutes.[49]

Surfactant Aggregation Numbers on Cotton. Aggregation numbers of fluorosurfactant were obtained by the two-site adsolubilization model using the parameters given in Table 2. The exact structure of the commercial surfactants were not known, so molecular weight of both surfactants were inferred based on assumptions for the number of carbon atoms and by comparison to a similar hydrocarbon surfactant CMC[53] with a fluoromethylene equated to 1.5 methylene units. An increase in the number of carbon atoms increases the length of the extended tail of surfactants but has relatively little effect on aggregation number estimation. Cross-sectional areas of a surfactant headgroup (A_s) and a monomer headgroup (A_a) were obtained from literature with similar headgroups.[53] From the aggregation number, the number of monomer molecules present in admicelles can be estimated.

Analysis with the two-site adsolubilization model yielded aggregation numbers from order 1 to 10^6. As the surfactant molecular density increases at solid/liquid interface, the sites

available in the core region increase and Γ_c dominates, so aggregation numbers rise. Fluorocarbon surfactant can adsorb both from aqueous and hydrocarbon media because of their thermodynamic stability.[54] Aggregation numbers were slightly higher for OFPM compared to TFEM for the zwitterionic surfactant (FS230), while the opposite was found for the cationic surfactant FS1620. The opposite trend for FS1620 is believed to be due to hydroxyl group of surfactant allowing water in admicelles, thereby facilitating adsolubilization of TFEM molecule.

From Figure 6, as the density of surfactant increased, the aggregation number calculated from the model almost followed a linear increasing trend on a log−log plot. Compared to aggregation numbers reported with hydrocarbon alcohols[31] and fluoroalcohols,[35] aggregation numbers for both the zwitterionic surfactant and cationic surfactant in this study were similar, ranging from 1 to 10 to over 10^6. Affinity between fluorocarbon−fluorocarbon compounds was stronger than hydrocarbon−hydrocarbon compounds because the formation of aggregates depends on the degree of interaction between the two compounds and hydrophobicity of fluoromonomers and lower headgroup charge of fluorosurfactants.[35,38] Aggregates of fluorosurfactants formed on the solid/water interface are stronger because of a strong C−F bond and electronegative fluorine that shields carbon.[55] Fluorinated surfactants are more surface active and more hydrophobic than their corresponding hydrogenated surfactant.[39]

■ CONCLUSION

Experimental measurement of adsorption and adsolubilization for fluorocarbon monomer-surfactant systems yield results consistent with the two-site adsolubilization model. A water-soluble monomer TFEM more effectively occupied peripheral sites. Partition coefficients and aggregation numbers were comparable to values observed for hydrocarbon and fluorocarbon alcohol−surfactant systems.

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Notes

The authors declare no competing financial interest.

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