

Adsorption of Anionic–Nonionic and Cationic–Nonionic Surfactant Mixtures on Kaolinite

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Received May 11, 1990; accepted September 18, 1990

Adsorption on Na-kaolinite from surfactant mixtures of nonionic octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) with the anionic sodium dodecyl sulfate ($C_{12}SO_4Na$) and the cationic dodecyltrimethylammonium chloride [$C_{12}(CH_3)_3NCl$] was studied in the surfactant concentration range varying from below CMC to above. It was found that in both systems, the adsorption of the ionic surfactant was enhanced by the presence of the nonionic surfactant and vice versa in the pre-CMC region. Chain–chain interaction between the adjacent ionic and nonionic surfactants on the particles has been proposed to be responsible for the enhanced adsorption. Such chain–chain interaction leads to the formation of surfactant clusters at the interface which abstract the hydrocarbon chains of the highly surface active $C_{12}EO_8$ into them. Under these conditions hydrophobicity of the particles as measured by skin flotation was found to be lower due to the exposed ethylene oxide groups. Decrease in the adsorption level of $C_{12}SO_4Na$ with increase in $C_{12}EO_8$ in the region above CMC has been attributed to the decrease of $C_{12}SO_4Na$ monomer concentration due to mixed micellization with $C_{12}EO_8$. The adsorption density of $C_{12}EO_8$ in plateau region passes through a maximum at equimolar ratio of the two surfactants. This has been suggested to be due to the most compact arrangement of surfactants in the cluster formed at the interface at the equimolar composition of the surfactants. Similar adsorption behavior from anionic–nonionic and cationic–nonionic surfactant mixtures suggests that the synergism arises mainly from the chain–chain interaction between the two surfactants in the adsorbed state. © 1991 Academic Press, Inc.

INTRODUCTION

Surfactant depletion due to adsorption on reservoir minerals and precipitation with dissolved cations is a major problem in chemical flooding for enhanced oil recovery (1). Use of mixtures of anionic and nonionic surfactants is receiving increasing attention since precipitation is significantly less in these systems (2). An understanding of the adsorption behavior of each surfactant component from mixtures is helpful for development of such application since chromatographic/selective adsorption will alter the compositional balance required for optimum oil recovery. Adsorption from surfactant mixtures on minerals such as alumina and silica has been reported in a few studies (3, 4). However, information on the adsorption on kaolinite, one of the major res-

ervoir minerals with more complex mineralogical composition and surface properties than either alumina or silica, has been scanty (5). Understanding of the adsorption mechanism from previous studies (5) was made difficult since adsorption was conducted only in the surfactant concentration range well above CMC and the nonionic surfactants used were polydispersed in nature.

In this work, adsorption of ionic–nonionic surfactant mixtures on kaolinite was studied using isomerically pure surfactants. Adsorption tests were carried out in a wide range of surfactant concentration varying from well below CMC to above. Since kaolinite possesses positive and negative sites (6, 7) adsorption characteristics of both cationic–nonionic and anionic–nonionic surfactant mixtures were studied to elucidate the role of electrostatic adsorption.

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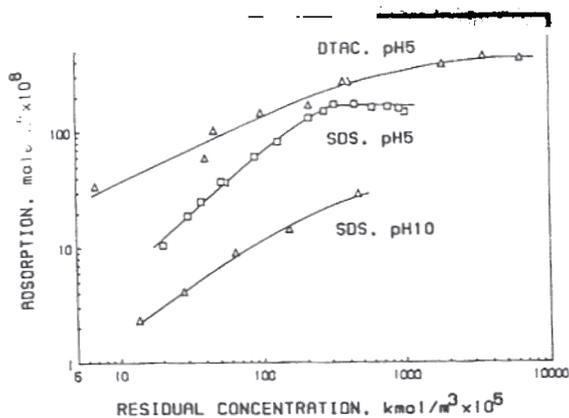


FIG. 1. Isotherms for sodium dodecyl sulfate and dodecyltrimethylammonium chloride adsorption on kaolinite. Ionic strength = 0.03 M NaCl, 25°C.

EXPERIMENTAL

Material

Well-crystallized Georgia kaolinite was purchased from the clay repository at the University of Missouri and was converted to Na-kaolinite by ion-exchange (8). Specific surface area of the sample obtained by nitrogen BET method using a Quantasorb was 8.2 m²/g.

The anionic sodium dodecylsulfate (C₁₂SO₄Na) and cationic dodecyltrimethylammonium chloride [C₁₂(CH₃)₃NCl] of >99% purity were purchased from Fluka Chemicals and Tokyo Kasai Chemicals, respectively. The nonionic octaethylene glycol mono-*n*-dodecyl ether, CH₃(CH₂)₁₁(OCH₂CH₂)₈OH or C₁₂EO₈, purchased from Nikko Chemicals, was of >97% purity. Since no minimum was found in the surface tension curves of these surfactants they were used as received.

Methods

Adsorption tests. Three gram samples of Na-kaolinite were contacted with 15 ml of 0.03 M NaCl solutions for 2 h in Teflon capped glass vials. Surfactant solutions of desired concentration were then added to make the total volume to 30 ml. The solids were conditioned with the surfactant by allowing

the suspension to stand for 72 h at room temperature (25 ± 2°C). The vials were periodically shaken manually every 24 h. The suspensions were then centrifuged and the supernatants were analyzed for residual surfactant concentration. Surfactant depletion from solution was used to calculate the adsorption density.

Sodium dodecyl sulfate concentration was determined using a two phase titration method (9, 10). Dodecyltrimethylammonium chloride concentration was determined by complexing the surfactant with excess C₁₂SO₄Na and measuring the noncomplexed C₁₂SO₄Na using the two phase titration method (9, 10). Analysis of octaethylene glycol mono-*n*-dodecyl ether (C₁₂EO₈) was conducted using a high pressure liquid chromatograph provided with a refractive index detector.

RESULTS AND DISCUSSION

Adsorption from Single Surfactant Solutions

Isotherms for the adsorption of anionic sodium dodecyl sulfate and cationic dodecyltrimethylammonium chloride are shown in Fig. 1, while that of the nonionic octaethylene glycol mono-*n*-dodecyl ether is given in Fig. 2. It can be seen from Fig. 1 that both the anionic C₁₂SO₄Na and the cationic C₁₂(CH₃)₃NCl adsorb on kaolinite at the same pH value. This

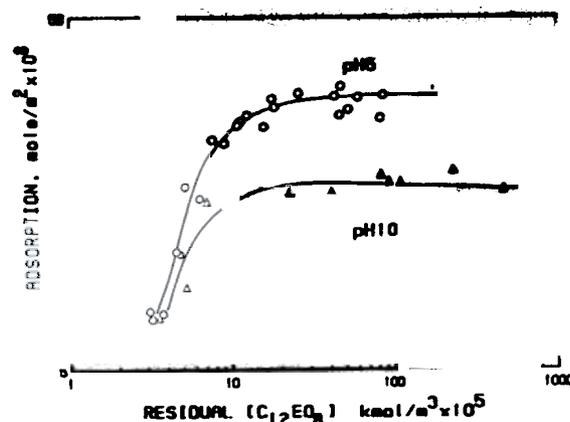


FIG. 2. Isotherms for octaethylene glycol mono-*n*-dodecyl ether on kaolinite. Ionic strength = 0.03 M NaCl, 25°C.

is consistent with an electrostatic adsorption mechanism for this system since both positive and negative sites coexist on kaolinite surface (6, 7). The above adsorption mechanism is also supported by the observed decrease in $C_{12}SO_4Na$ adsorption as the pH is increased from 5 to 10, since the number of positive sites on kaolinite does decrease with increasing pH (6, 7).

Further examination of the isotherms shows that the saturation adsorption density in the case of cationic $C_{12}(CH_3)_3NCl$ is 4.35×10^{-6} mol/m² which coincides with the monolayer capacity (4.37×10^{-6} mol/m²) calculated based on a cross-sectional area of 38 \AA^2 (11). This suggests that the cationic surfactant adsorbs not only on the negative sites but also covers the positive sites indicating the possibility of two-dimensional condensation. Such a mechanism for cationic surfactant adsorption has also been suggested by Cases *et al.* (12). In the case of anionic $C_{12}SO_4Na$ the surface coverage at plateau, calculated based on a cross-sectional area of 53 \AA^2 (11), is 56% which indicates that about half of the surface is covered by positive sites.

It has been reported by Cases *et al.* (12) that the positive sites are present only on the broken edges and that even in most crystalline samples the broken edges constitute only 40% of the total surface area. Since the surface coverage of the anionic $C_{12}SO_4Na$ is estimated to be above 50% it appears that part of the surfactant adsorbs on negative sites through Na^+ counter ions (13) or positive sites are present also on the basal faces. The positive sites on basal faces can arise from the precipitation of dissolved aluminum hydroxide complexes.

It can be seen from Fig. 2 that the adsorption density of octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$), as in the case of sodium dodecyl sulfate ($C_{12}SO_4Na$), also decreases with an increase in pH. Similar decrease in adsorption with increase in pH has been reported for poly(ethylene) oxide (PEO) on silica (14). This similarity coupled with the fact that the ethylene oxide groups are the common hydrophilic moiety for both PEO and $C_{12}EO_8$

would suggest a hydrogen bonding mechanism for $C_{12}EO_8$ adsorption as proposed for PEO (14) and nonionic TX-100 (15) adsorption on silica. Reduced adsorption at higher pH values can be attributed to the deprotonation of the surface hydroxyl groups (16, 7) which will result in a decrease in the number of hydrogen bonding sites available for $C_{12}EO_8$ adsorption. Using a molecular cross-sectional area of 65 \AA^2 (11) for $C_{12}EO_8$ in the adsorbed state, the surface coverage at saturation can be calculated to be 12% which would also represent the percentage of the kaolinite surface covered by groups capable of hydrogen bonding with the nonionic surfactant.

An important inference that can be drawn from the adsorption studies discussed above is that, unlike alumina which barely adsorbs ethoxylated alcohols (3), and silica which adsorbs ethoxylated alcohol (3) but not $C_{12}SO_4Na$, kaolinite $[(Al(OH)_2)_2 \cdot O \cdot (SiO_2)_2]$, adsorbs both $C_{12}SO_4Na$ and $C_{12}EO_8$ to about the same order of magnitude indicating that the kaolinite surface exhibits the characteristics of both alumina and silica with respect to the adsorption of these surfactants.

Adsorption from Surfactant Mixtures

The effect of mixing the ionic (anionic and cationic) and nonionic surfactants on the adsorption behavior of individual components is shown in Figs. 3–7. The isotherms in these figures have been divided in two regions below and above mixed CMCs of the solution, in order to facilitate explanation of the results.

Anionic-nonionic surfactants system. Adsorption isotherms. Preplateau region: The isotherms for the adsorption of sodium dodecyl sulfate ($C_{12}SO_4Na$) from mixtures of different composition are shown in Fig. 3, while those of octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) are plotted in Fig. 4. It can be seen from Fig. 3 that the affinity of $C_{12}SO_4Na$ to the surface is enhanced by the presence of $C_{12}EO_8$ as indicated by the continuous shift of $C_{12}SO_4Na$ isotherms toward the left with increase of the molar ratio of $C_{12}EO_8$. This

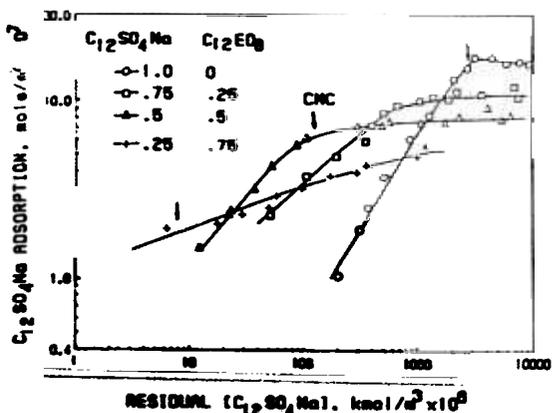


FIG. 3. Isotherms for the adsorption of $C_{12}SO_4Na$ from $C_{12}SO_4Na/C_{12}EO_8$ mixtures on kaolinite. Ionic strength = $0.03 M NaCl$, pH 5, $25^\circ C$. Arrows indicate critical micelle concentration of the corresponding surfactants.

can be explained in terms of the coadsorption of $C_{12}SO_4Na$ and $C_{12}EO_8$ as shown schematically in Fig. 8; $C_{12}SO_4Na$ adsorption is assisted, in addition to its electrostatic interaction with the positive sites on kaolinite, by the chain-chain interaction with $C_{12}EO_8$ adsorbed on adjacent sites. Because of the free energy gain from such chain-chain interactions the residual concentration, or the chemical potential, of $C_{12}SO_4Na$ required to achieve a cer-

tain level of adsorption is reduced resulting in a shift of the isotherm toward the left.

Another feature to be noted on the sodium dodecyl sulfate ($C_{12}SO_4Na$) adsorption isotherm is the decrease in the slope of the isotherm as the molar ratio of octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) is increased. For adsorption of pure $C_{12}SO_4Na$ on kaolinite, a slope of 1 is obtained on a logarithmic plot, indicating the absence of lateral chain-chain interactions (18). A value less than 1 for the slope, as seen in Fig. 3, suggests electrostatic hindrance for $C_{12}SO_4Na$ adsorption resulting possibly from the masking of the positive sites by adsorbed ethylene oxide chains (Fig. 8b).

The adsorption of $C_{12}EO_8$, similar to that of $C_{12}SO_4Na$, is enhanced by the presence of $C_{12}SO_4Na$ as seen from a continuous shift in the isotherm to the left with increase in the molar ratio of $C_{12}SO_4Na$. This can again be attributed to the chain-chain interaction between $C_{12}SO_4Na$ and $C_{12}EO_8$. It is conceivable that due to chain-chain interaction between adsorbed $C_{12}SO_4Na$ and $C_{12}EO_8$, mixed surfactant clusters will be formed at the interface. These mixed surfactant clusters, serving as hydrophobic pools, can enhance the adsorption of $C_{12}EO_8$ by abstracting the hydrocarbon

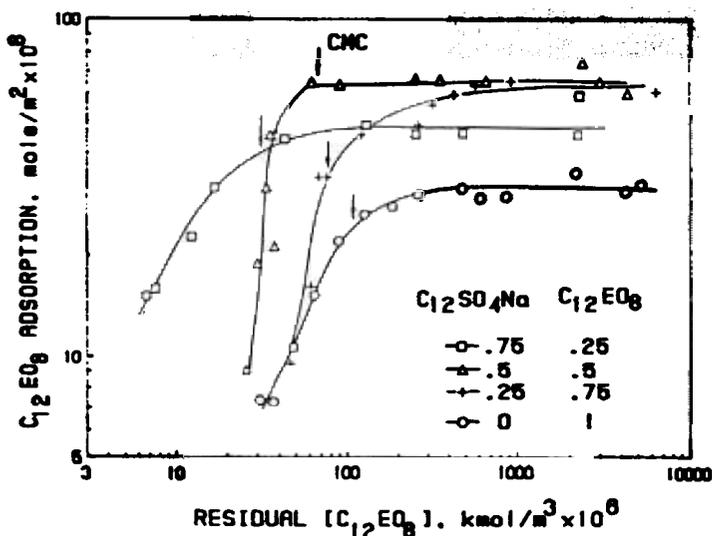


FIG. 4. Isotherms for the adsorption of $C_{12}EO_8$ from $C_{12}SO_4Na/C_{12}EO_8$ mixtures on kaolinite. Ionic strength = $0.03 M NaCl$, pH 5, $25^\circ C$.

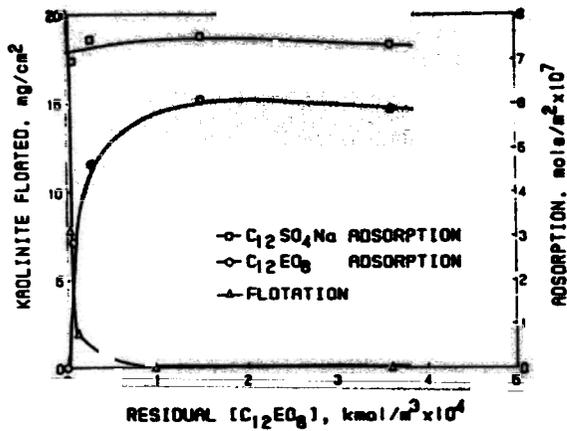


FIG. 5. Skin flotation of kaolinite after mixed surfactant adsorption. $C_{12}SO_4Na$ concentration fixed at 1.0 mM. Ionic strength = 0.03 M NaCl, 25°C, pH 5.

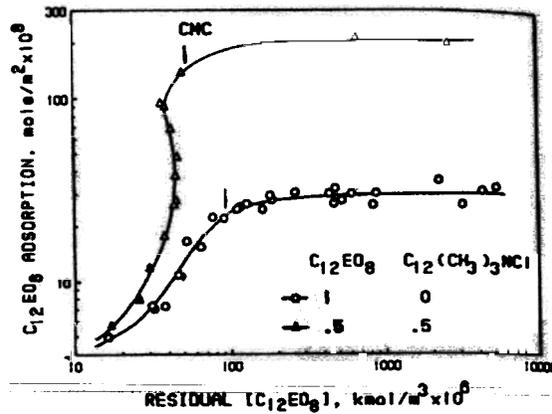


FIG. 7. Isotherms for $C_{12}EO_8$ adsorption on kaolinite from $C_{12}(CH_3)_3NCl/C_{12}EO_8$ mixtures. Ionic strength = 0.03 M NaCl, pH 4.5–5, 25°C.

chains of the highly surface active nonionic surfactant into the clusters leaving the ethylene oxide segments protruding into the bulk solution, as shown schematically in Fig. 8c.

Adsorption isotherms. Plateau region. It can be seen from Fig. 3 that in plateau region (above CMC) the adsorption of sodium dodecyl sulfate ($C_{12}SO_4Na$) while alone reaches a plateau, whereas in the presence of octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) it continues to increase even above CMC. This is because in mixed surfactant systems, unlike in single surfactant solutions, the monomer concentration of anionic surfactant does in-

crease above CMC, while that of nonionic surfactant does decrease (3, 19). A consistent decrease of $C_{12}SO_4Na$ adsorption in plateau region is observed as the molar ratio of $C_{12}EO_8$ in the mixture is increased. This can be attributed to (a) reduced $C_{12}SO_4Na$ monomer concentration due to mixed micellization with $C_{12}EO_8$ as indicated by the decrease in CMC with increase in the molar ratio of $C_{12}EO_8$ and (b) masking of the positive sites that are responsible for $C_{12}SO_4Na$ adsorption by the ethylene oxide chains of the adsorbed $C_{12}EO_8$.

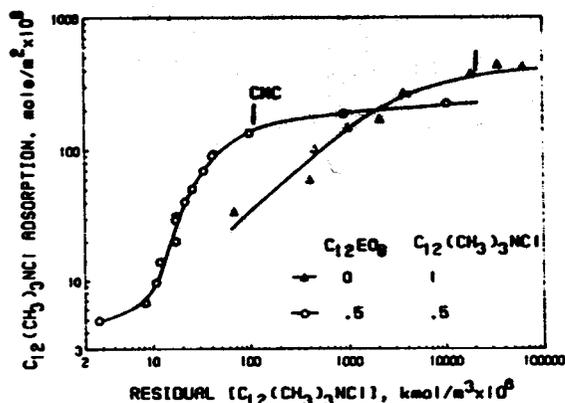


FIG. 6. Isotherm for dodecyltrimethylammonium chloride adsorption on kaolinite from $C_{12}(CH_3)_3NCl/C_{12}EO_8$ mixtures. Ionic strength = 0.03 M NaCl, pH 4.5–5, 25°C.

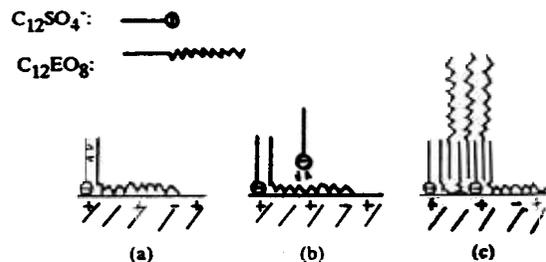


FIG. 8. Schematic representation of the mechanism of surfactant adsorption on kaolinite. (a) Chain-chain interaction between adjacent $C_{12}SO_4Na$ and $C_{12}EO_8$ molecules results in enhanced adsorption in the lower concentration range (pre-CMC region) for both surfactants; (b) electrostatic hindrance for further $C_{12}SO_4Na$ adsorption results from the masking of positive sites on kaolinite by ethylene oxide chain adsorption; (c) formation of mixed surfactant clusters and abstraction of $C_{12}EO_8$ hydrocarbon chains into the clusters.

In the case of the nonionic surfactant, since the monomer concentration does decrease with increase in the total surfactant concentration (3, 15), the isotherm of octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) will be expected to pass through a maximum at the CMC of mixed surfactants. However, it can be seen from Fig. 5 that $C_{12}EO_8$ adsorption isotherms in plateau region are either flat or have a positive slope. This is attributed to the increased affinity of $C_{12}EO_8$ toward the surface modified by the adsorbed $C_{12}SO_4Na$. As can be seen from Fig. 3, the adsorption of $C_{12}SO_4Na$ increases even above mixed CMC. The effect of such continued modification of the interface by $C_{12}SO_4Na$ adsorption apparently outweighs the effect of decrease in $C_{12}EO_8$ monomer concentration. It is also seen from Fig. 4 that the plateau adsorption density value of $C_{12}EO_8$ is, in all cases, enhanced by the presence of $C_{12}SO_4Na$. Such an enhancement can be accounted for, as explained earlier, by the abstraction of additional $C_{12}EO_8$ chains into the mixed surfactant clusters at the interface (see Fig. 8c). Such hydrocarbon chain abstraction is apparently highly dependent on the organization of the mixed surfactant clusters at the interface and therefore maximum adsorption increase occurs at a certain molar ratio between the two surfactants. As is seen in Fig. 4, the maximum $C_{12}EO_8$ adsorption in plateau region occurs at about 1:1 molar ratio between $C_{12}SO_4Na$ and $C_{12}EO_8$. The dependence of $C_{12}EO_8$ hydrocarbon chain abstraction on the organization of mixed surfactant clusters is also revealed by the change in slope of the $C_{12}EO_8$ isotherms in preplateau region. As seen in Fig. 4, the slope of the adsorption isotherm increases in the presence of $C_{12}SO_4Na$ with the maximum slope occurring around 1:1 molar ratio, indicating a more compact arrangement of the adsorbed surfactants in the cluster, which eventually leads to maximum $C_{12}EO_8$ abstraction as shown by the highest plateau adsorption density value at this ratio.

The theory of abstraction of hydrocarbon chain of octaethylene glycol mono-*n*-dodecyl

ether ($C_{12}EO_8$) into the hydrophobic pool formed by the clusters of mixed surfactant is also supported by the (skin) flotation results. Since such an abstraction would result in orientation of ethylene oxide chains toward the bulk, the floatability of kaolinite decreases as the adsorption of $C_{12}EO_8$ is increased in the presence of $C_{12}SO_4Na$ (Fig. 5).

Cationic-nonionic surfactants system: Adsorption tests for this system were carried out at 1:1 molar ratio of the two surfactants. It can be seen from Figs. 6 and 7 that the isotherms obtained for the adsorption of cationic dodecyltrimethylammonium chloride ($(C_{12}(CH_3)_3NCl)$) and nonionic octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) exhibit features similar to that found for $C_{12}SO_4Na$ - $C_{12}EO_8$ system indicating that the adsorption mechanism is the same for both systems.

CONCLUSIONS

Synergistic interaction between surfactants was observed during the adsorption on kaolinite for both anionic-nonionic and cationic-nonionic surfactant mixtures. In these binary surfactant systems, affinity of the ionic and the nonionic surfactant toward the surface was found to be enhanced by the presence of one another in the pre-CMC region. Increased chain-chain interaction and the formation of mixed surfactant clusters have been proposed to be the main reasons for the observed synergism. Above CMC, sodium dodecyl sulfate ($C_{12}SO_4Na$) adsorption decreased with increasing octaethylene glycol mono-*n*-dodecyl ether ($C_{12}EO_8$) composition and this was attributed to the decrease in $C_{12}SO_4Na$ monomer because of the decrease in CMC for the mixed surfactants. The abstraction of hydrocarbon chains of $C_{12}EO_8$ into the hydrophobic pools formed by mixed surfactant clusters is proposed to be responsible for the observed adsorption increase above mixed CMC. Hydrophobicity of the particle was found to be lowered under such conditions due to the orientation of the ethylene oxide chains in the bulk solution. Such abstraction is apparently

dependent on the organization of the surfactants in the cluster and was therefore dependent on the composition of the surfactant mixtures with the maximum abstraction of $C_{12}EO_8$ occurring at the equimolar ratio of the surfactants. Similarities observed between the anionic-nonionic and the cationic-nonionic surfactant mixtures suggest that the synergism observed in mixed surfactant system is mainly due to hydrophobic interactions between the hydrocarbon chains of the ionic and the non-ionic surfactants.

ACKNOWLEDGMENTS

Financial support of the National Science Foundation (NSF Contract NSF-CBT-86-15524-A02), Department of Energy (DOE Contract DE-FG22-89BC14432), Unilever Research, Engelhard, and Standard Oil Company of Ohio is gratefully acknowledged.

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