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Self-Desorption of Mixtures of Anionic and Nonionic Surfactants from a Silica/Water Interface

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The adsorption of a mixture of two surfactants, the anionic sodium dodecyl sulfate and the nonionic nonylethylene glycol *n*-dodecyl ether, from water to a hydrophilic silica dispersion has been studied at pH = 5.0 and 25 °C in a large concentration range at several surfactant compositions by a classical depletion method. The adsorption of the latter compound onto silica induces the incorporation of the former by the formation of mixed surfactant aggregates. However, at high total surfactant concentration, about 100 times the mixed critical micelle concentration, both surfactants are partially desorbed from the silica surface. This behavior is qualitatively interpreted as the consequence of two phenomena: on one hand, the strong interaction between the anionic and the nonionic surfactant in the bulk above the critical micelle concentration and on the other hand the repulsion which occurs between the negatively charged dissociated silanol groups and the anionic surfactant in the mixed aggregates at the silica/water interface. At high total surfactant concentration and above a specific anionic/nonionic surfactant ratio the former phenomenon is favored over the latter, hence the desorption of both surfactants.

Introduction

The properties of mixtures of surfactants have been thoroughly studied in recent years, and monographs have provided much interesting and useful information especially in the case of bulk aqueous solution.[1,2] The interpretation of these binary surfactant solutions with thermodynamic models is still an active field of interest.[3,4] Surfactants are well-known to adsorb at solid/liquid interfaces. In the case of mineral oxides, ionic surfactants generally do not adsorb on a substrate of like charge. Hence cationic surfactants do not adsorb on alumina below the isoelectric point of 9.1 and likewise anionic surfactants do not adsorb on silica above a pH of about 2.5, the isoelectric point of that substrate. Exceptions to this general rule have been discussed in the literature.[5,6] It is also well-known that nonionic surfactants such as alkylethoxylated compounds adsorb readily on silica but not on alumina, at least not to any great extent. To overcome these chemical specificities, mixtures of surfactants may be used. For example, in the case of a positively charged alumina, an adsorbed anionic surfactant will incorporate the nonadsorbing nonionic surfactant by a mechanism which may be looked upon either as the formation of adsorbed mixed surfactants aggregates as obtained in the bulk or as an adsolubilization effect.[7,8] Conversely, the nonionic surfactant adsorbed on a negatively charged hydrophilic silica will incorporate a nonadsorbing anionic surfactant by the same mechanisms although both surfactant and solid substrate are of like charges.[9–12] The pH of the system may be varied in order to control such mechanisms. For example, a nonionic surfactant may be incorporated to an alumina/water interface by a cationic surfactant if the pH of the system is raised to about 10, where the mineral oxide surface is predominantly negatively charged.[13] Finally, the case where both surfactants (a cationic and a nonionic alkylethoxylated) of a binary mixture compete for the adsorption onto a silica/water interface has also be considered.[14,15]

It is generally accepted that the adsorption of surfactants from water to a hydrophilic mineral oxide dispersion can be looked upon along the following pattern: at low surfactant coverage, individual molecules adsorb flat on preferential polar sites. As the concentration increases at constant pH and ionic strength, small aggregates begin to form, the structure of which (hemimicelles, admicelles, micelle-like aggregates) depends on the type of surfactants, the type and the surface properties of the substrate, and the pH of the solution. Most certainly, micelle-like aggregates are formed with nonionic surfactants[16] whereas hemimicelles or admicelles are favored with ionic surfactants. At concentrations close to, and sometimes above, the critical micelle concentration (cmc), a plateau value is observed corresponding to the solid substrate saturation.

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Free micelles begin to form which are believed not to adsorb at the solid/water interface. This general picture should apply also to mixed surfactants although the details of the mechanism are known for only a few cases from neutron scattering experiments.[15]

In the investigations recalled above, the free micelles do not adsorb at the solid/water interface and the adsorbed aggregates remain at that interface as the concentration is increased above the cmc. It is one of the purposes of this study to show that at least for mixed anionic/nonionic surfactant mixtures a partial desorption from a silica/water interface may be observed upon increasing surfactant concentration well beyond the cmc, a phenomenon which has not be previously described.

The anionic surfactant used was a monodispersed sample of sodium dodecyl sulfate (SDS) while the nonionic surfactant was a polydispersed compound, nonylethylene glycol n-dodecyl ether ($C_{12}E_9$). Silica was a very pure hydrophilic dispersion.

Materials and Methods

SDS was from Sigma (France) with a purity above 99%. Surface tension measurements (Kruss, model K10T) showed no signs of a minimum around the cmc. $C_{12}E_9$ was a pure, polydispersed compound (Nikko chemicals, Japan) with an average degree of ethoxylation of 8.7. Sodium chloride was a 99% pure compound from Aldrich (France). These compounds were used without purification. The silica was a hydrophilic dispersion 99.8% pure. It was a gift from Degussa (France). Its specific (BET) surface was 200 ± 25 m²/g.

The standard batch technique employed was as follows: The nonionic surfactant, pure or mixed at a constant ratio with SDS, was equilibrated in a thermostat at 25 °C for 24 h with 10 g/L of silica and NaCl at concentrations of either 0.04 or 0.1 mol/L. The pH of the inhomogeneous solution was adjusted at pH = 5.0 $\pm$ 0.05 after 6 h of equilibration with NaOH at 0.5 mol/L (pH-meter from Beckman, USA). The solutions were centrifuged at 8500g for 45 min on a Sigma 4K-15 (Fisher Bioblock, France) at 25 °C.

The supernatant was analyzed by high-performance liquid chromatography (HPLC) for each surfactant. When the concentrations were high enough, a RID-6A differential refractometer was employed (Touzart and Matignon, France) and the solutions were injected in a System Gold HPLC chromatographic device (Beckman, USA) as described previously.[17]

In the case of trace amounts of either surfactants, enrichment procedures were used before chromatographic analysis. The nonionic surfactant was extracted on C_{18} bonded silica in order to retain the nonionic compound (Sep-Pak plus C_{18}, Waters, France). For SDS, a cartridge for anion exchange was used (Sep-Pak Accell plus QMA, Waters, France). All experimental details are provided in a previous publication.[17]

The cmc of the mixed surfactants were calculated from the Clint–Rubingh[18,19] theory knowing the cmc of the single compounds and the regular solution interaction parameters (Table 1). The relevant equation may be found in several publications and need not be repeated here. It is well-known that because of the screening effect of the ionic aggregates by the added salt, the interaction between the two surfactants decreases. This fact is well encountered for by the less negative value of the interaction coefficient β displayed in Table 1. These binary interaction parameters which are derived from the regular solution model as applied to mixed surfactant systems incorporate all nonideal terms of free energy of mixing of the two surfactants.[19] It is noteworthy that the charged screening of the sodium salt on the mixed micelles is diminished to the extent that the usual decrease of the cmc with added common salt is not predicted by the Clint–Rubingh theory.

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Table 1. Solution Parameters for the Clint–Rubingh Theory of Mixed Surfactant Solutions

	$C_{12}E_9$ (mol/L) $\times 10^5$	SDS (mol/L) $\times 10^3$	β^a
cmc without salt	8.5^b	7.9^c	-4.1^d
cmc with 0.04 M NaCl^c	8.0	3.6^c	-2.8^e

^{a} Note: The β values used in the calculations were taken from data on SDS/C_mE_n systems very close to the present one: $n = 8^d$ and $n = 6.^e$ As the dependence of β upon the number of ethoxy groups for a constant hydrocarbon chain m ($m = 12$) with n values between 6 and 10 is very small, the chosen values were considered as appropriate enough for the evaluation of the cmc of the present binary system. ^{b} Jiding, X.; Zhengyu, H. In *Surfactants in solution*; Mittal K. L., Bothorel, P., Eds.; Plenum Press: New York, 1986; p 1055. ^{c} Jacquier, J. C.; Desbène, P. L. *J. Chromatogr., A* **1995**, *718*, 167. ^{d} Rosen, M. J. In *Phenomena in mixed surfactant systems*; Scameborn, J. F., Ed.; ACS Symposium series 311; American Chemical Society: Washington, DC, 1986; p 144. ^{e} Penfold, J.; Staples, E.; Thompson, L.; Tucker, I.; Hines, J.; Thomas, R. K.; Lu, J. R. *Langmuir* **1995**, *11*, 2496.
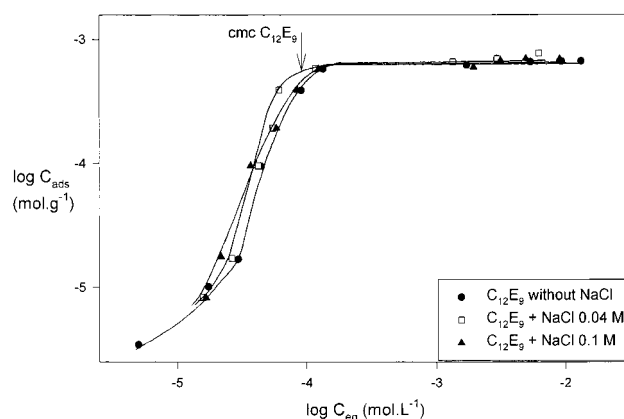

Figure 1. Adsorption isotherm of the nonionic surfactant $C_{12}E_9$ on silica in the present of added salt.

Results and Discussion

A. Initial Observations. Although the adsorption of alkylpoly(oxyethylene) surfactants on silica has been well characterized in a number of studies, the main results will be recalled in the case of $C_{12}E_9$. The adsorption isotherm is presented in Figure 1 on a log/log scale. As the effect of sodium chloride will be examined in the case of the anionic/nonionic surfactant mixtures, it is also displayed on that figure. The profiles of the adsorption isotherm observed are classical as outlined in the Introduction. Small differences may be observed in the isotherm with the addition of NaCl below the cmc, but these differences are small and in any case disappear above the cmc. Furthermore, as expected, the onset of the adsorption plateau corresponds to the cmc of the surfactant.

Figure 2 presents the global isotherm of the three $C_{12}E_9$/SDS mixtures investigated with constant ratios of 0.7/0.3, 0.5/0.5, and 0.3/0.7. In all cases, the adsorption increases with surfactant concentration and attains a plateau value. The presence of the nonionic surfactant at the silica/water interface induces the incorporation of the anionic surfactant. Repeated experiments with SDS alone at pH = 5.0 had confirmed that no measurable adsorption of that surfactant occurs onto the silica dispersion. One recalls that silica particles are negatively charged above a pH value of about 2.5. The nonadsorption of SDS in the absence of $C_{12}E_9$ was therefore an expected result due to the Coulomb repulsion between the negatively charged anionic surfactant and the silica surface.

Let us consider first the $C_{12}E_9$-rich mixture with ratio 0.7/0.3. A classical sigmoid profile is observed with an
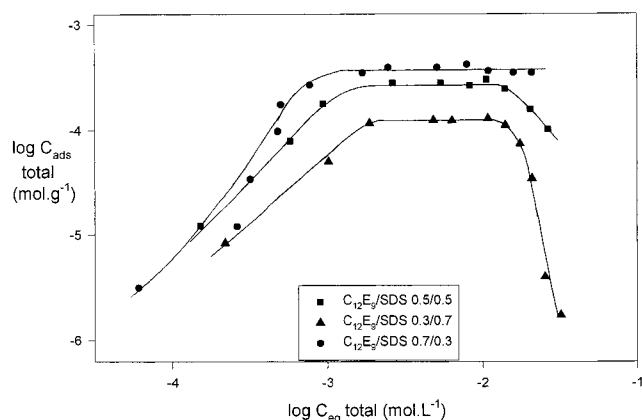
Figure 2. Global adsorption isotherms of three $C_{12}E_9$/SDS mixtures on silica in the absence of added salt.

Table 2. Some Characteristic Parameters for Single and Mixed Surfactant Solutions at the Silica/Water Interface

systems[a]	cmc (mol/L)	Plateau onset (mol/L)	Γ_{max} (mol/g)
single surfactants			
$C_{12}E_9$	8.5×10^{-5}	8.5×10^{-5}	6.8×10^{-4}
$C_{12}E_9$ + NaCl (4×10^{-2})	8.0×10^{-5}	7.2×10^{-5}	6.9×10^{-4}
SDS	7.9×10^{-3}		0
SDS + NaCl (4×10^{-2})	3.6×10^{-3}		0
$C_{12}E_9$/SDS (0.7/0.3)			
a. NaCl = 0	1.0×10^{-4}		
$C_{12}E_9$		3.0×10^{-5}	2.5×10^{-4}
SDS		1.7×10^{-3}	5.0×10^{-5}
b. NaCl = 4.0×10^{-2}	1.1×10^{-4}		
$C_{12}E_9$		1.4×10^{-5}	2.4×10^{-4}
SDS		6×10^{-4}	1.5×10^{-4}
$C_{12}E_9$/SDS (0.5/0.5)			
NaCl = 4.0×10^{-2}	1.4×10^{-4}		
$C_{12}E_9$		8.9×10^{-6}	1.3×10^{-4}
SDS		1.4×10^{-3}	1.3×10^{-4}
$C_{12}E_9$/SDS (0.3/0.7)			
NaCl = 4.0×10^{-2}	2.0×10^{-4}		
$C_{12}E_9$		7.1×10^{-6}	5.0×10^{-5}
SDS		1.6×10^{-3}	6.8×10^{-5}

[a] Concentrations expressed in mol/L.

adsorption plateau. However, with the other two surfactant binaries, a new behavior is observed: at constant composition ratio, surfactant adsorption decreases above a total equilibrium concentration of about 0.02 M. Note that the cmc of these surfactant mixtures as calculated using the Clint–Rubingh theory with the constants of Table 2 are equal to 1.1×10^{-4}, 1.4×10^{-4}, and 2.0×10^{-4} mol/L for the 0.7/0.3, 0.5/0.5, and the 0.3/0.7 binaries, respectively. Thus, the surfactant desorption begins at a total surfactant concentration which is higher by a factor of over 100 than that of the cmc.[20] In fact, the onset of the adsorption plateau for the surfactant mixture corresponds, in all three cases, to the value obtained with the surfactant with the highest cmc, i.e., SDS. This observation had been made before in the case of mixtures of nonionic surfactants with cmc values different from each other by a factor of about 100.[20] This situation is close to that encountered with the present chemical system.

The nonionic-rich mixture with a 0.7/0.3 ratio seems to be too large for the decrease to be observed or, alternatively, it would have been observed even at that surfactant ratio if still higher total surfactant concentration had been investigated.
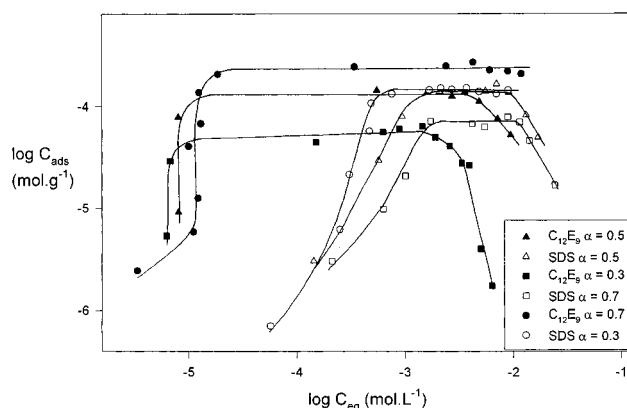
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Figure 3. Individual adsorption isotherms for $C_{12}E_9$ and for SDS in three different mixture composition on silica in the absence of added salt.

The desorption at higher surfactant concentrations of both components of the mixtures for the 0.5/0.5 and 0.3/0.7 ratios has not been reported by previous investigators who have been dealing with the adsorption of ionic/nonionic surfactant mixtures on solid/water interfaces. It seems that the reason is that the concentration domain investigated was too small and, in any case, smaller than that in the present study. Recall also that the mixture composition is an important factor for this decreased adsorption to be observed. However, the hypothesis has been put forward by Wang and Kwak[21] for mixtures of SDS coadsorbed with Triton X-100 on alumina.

Xu and Somasundaran[11] in the case of a $C_{12}E_8$/SDS mixture adsorbed on kaolinite have indeed observed a decrease of adsorption of the nonionic surfactant as this surfactant concentration was increased. But the experimental conditions were entirely different from ours. Xu and Somasundaran experiments had been performed at *constant SDS concentration.* These conditions are those which are employed in order to illustrate the so-called adsolubilization effect.[22] As SDS concentration was constant, the anionic molecules were first incorporated (adsolubilized) to the nonionic aggregates which were adsorbed at the kaolinite/water interface below the mixed cmc. Above the cmc, free micelles are formed and as the SDS concentration was maintained constant and the $C_{12}E_8$ concentration continued to increase, the anionic surfactant molecules were distributed between the adsorbed aggregates on kaolinite and the free micelles. Thus, as more free micelles were formed, SDS was solubilized in the mixed micelles, hence the decreased adsorption from the kaolinite/water interface. The situation presented in the present investigation is different, as the *ratio of surfactants is maintained constant* as the total surfactant concentration increases.

It was of course of interest to determine the isotherm of SDS and of $C_{12}E_9$ in the various surfactant mixtures even without consideration of the polydispersity of the nonionic component. This aspect will be considered in a separate report. The results are presented on Figure 3. The surfactant adsorption begins at the lowest concentrations for $C_{12}E_9$. The isotherms at the highest surfactant concentrations concern SDS, the component with the largest cmc. It is observed that none of the surfactants desorbs in the concentration domain investigated at a ratio of 0.7/0.3, i.e., in the $C_{12}E_9$-rich mixture. However, for the 0.5/0.5 mixture, *both* surfactants are desorbed from the

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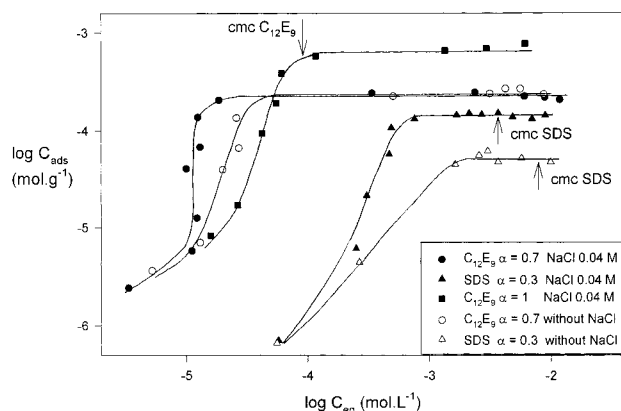(22) Monticone, V.; Mannebach, M. H.; Treiner, C. *Langmuir* **1994**, *10*, 2395.

Figure 4. Effect of salt on the individual adsorption isotherms on silica of a (0.7/0.3) $C_{12}E_9$/SDS mixture.

silica/water interface at higher surfactant concentrations, a behavior which is further enhanced with the SDS-rich mixture.

The reason for this behavior can be qualitatively understood along the following lines. It is well-known that in bulk solutions SDS interacts rather strongly with alkyl-(poly)oxyethylene surfactants. This is quantitatively shown by the relatively large negative interaction parameter of the regular solution approximation (see Table 1). Furthermore, SDS is repelled from the silica surface by the negatively charged silanol surface groups as recalled above (at pH = 5.0 of the experiments). Thus, as the proportion of the repelled SDS molecules becomes larger than that of the $C_{12}E_9$ molecules which retain these SDS molecules from going into the micellar solution, the latter phenomenon overcomes the former one. Put differently this means that if there was a possibility to determine an interaction parameter β of the regular solution approximation between the two surfactants *at the silica/water interface,* it should be found less negative than that in the bulk.

The effect of the adsorption of SDS on that of $C_{12}E_9$ shows some interesting characteristics. Let us consider the 0.7/0.3 surfactant ratio without added salt (Figure 4). The presence of the anionic surfactant actually increases the adsorption of the nonionic from low surfactant coverage up to the plateau onset. However at this maximum surfactant coverage, the presence of SDS decreases the maximum adsorption of the nonionic component by about 50%. This effect had been reported previously by Xu and Somasundaran[11] for a 0.5/0.5 SDS/$C_{12}E_8$ mixture adsorbed on silica. It should be considered as the result of the strong interactions between the two surfactants. Calculations with the Clint−Rubingh theory indicate that at low surfactant concentration for such mixtures in the bulk, the aggregate contains more of the nonionic component than predicted by the stoichiometric composition. This is mostly due to the difference of cmc's of the two components. As the concentration increases, the aggregate composition approaches the stoichiometric one. Applied qualitatively to the present situation (at the silica/surface), this would mean that the mixed aggregates contain more SDS molecules per aggregate at the plateau than at low surfactant coverage. Hence the−relatively−lower adsorption of the mixed aggregates at the plateau is the consequence of the larger repulsion between that surfactant and the silica surface.

It is also of interest to examine the effect of added NaCl on the adsorption isotherms. This was considered in the case of the 0.7/0.3 system only (Figure 4). The presence of salt increases the adsorption of SDS (by about 65%) as
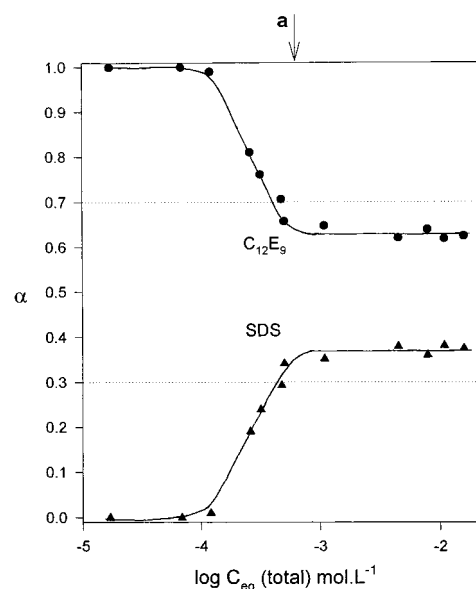

Figure 5. Variation of the surface composition of aggregates adsorbed on silica as a function of total equilibrium concentration for the $C_{12}E_9$/SDS (0.7/0.3) system. The arrow (a) marks the onset of the adsorption plateau. No desorption was observed.

expected from the classical screening effect observed by the addition of a neutral salt. However the nonionic component adsorption is also increased in the presence of NaCl below the adsorption plateau which is not the case in the absence of SDS (see Figure 1). One could assume therefore, in agreement with others,[23] that the screening effect of NaCl on the SDS monomers induces an extra hydrophobic environment for the nonionic surfactant again as in the case of the SDS/nonionic polymer case, hence the increased adsorption.

B. Surface Composition of the Mixed Adsorbed Aggregates. The composition of the adsorbed aggregates may be obtained from the present data and provide additional information to the adsorption behavior of these mixed surfactants at the solid/water interface.

Below the cmc, only monomers are found in the supernatant. Above the mixed cmc, the supernatant contains both the surfactant monomers and the mixed micelles of SDS and $C_{12}E_9$. The chromatographic method permits calculation of the individual equilibrium concentration of each of the surfactants in the aqueous solution. With knowledge of the initial concentration, the surface concentration can be unambiguously obtained by differences between initial and supernatant concentrations for each surfactant.

Figures 5, 6, and 7 present the results obtained below and above the cmc for both SDS and $C_{12}E_9$. The onset of the adsorption plateau is marked by the first arrow on these graphs. The second arrow indicates the onset of the desorption process. Note that the abcissa represents the *total equilibrium surfactant concentration* as on Figure 2. The variation of surfactant monomers in the inhomogeneous system cannot be deduced from the present experiments as monomers and micelles concentrations evidently cannot be analyzed independently.

Figure 5 presents the composition of the adsorbed aggregates for the $C_{12}E_9$-rich (0.7/0.3) mixture. The SDS molecules are incorporated to the silica/water interface at a threshold concentration only when the nonionic component begins to form adsorbed micellar-like aggregates. A concomitant decrease of the adsorption of the
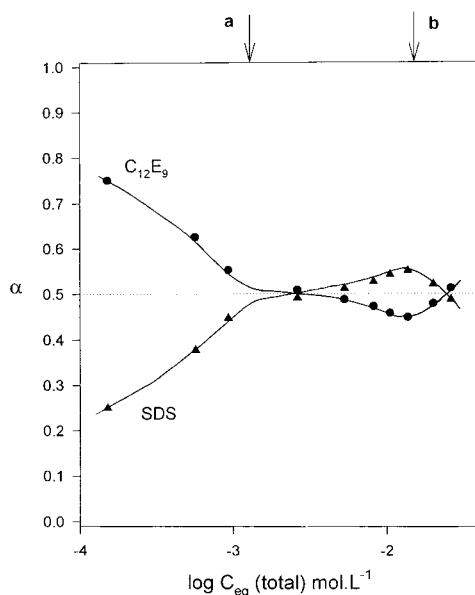
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Figure 6. Variation of the surface composition of aggregates adsorbed on silica with total equilibrium concentration for the $C_{12}E_9$/SDS (0.5/0.5) system. The onset of the adsorption plateau is marked by the first arrow (a). The second arrow (b) indicates the onset of the desorption process

Figure 7. Variation of the surface composition of aggregates adsorbed on silica with total equilibrium concentration for the $C_{12}E_9$/SDS (0.3/0.7) system. The onset of the adsorption plateau is marked by the first arrow. The second arrow indicates the onset of the desorption process

nonionic component is observed at maximum surfactant coverage as noted above. Above the plateau onset, the composition of the mixed adsorbed aggregates remains constant.

For a stoichiometric composition of 0.5/0.5 (Figure 6), or 0.3/0.7, (Figure 7) the threshold concentration for the incorporation of SDS molecules is not as clear-cut as in the previous mixture. The fraction of SDS in the mixed aggregates is increased and that of $C_{12}E_9$ is decreased when compared to the $C_{12}E_9$-rich mixture, as expected, which does not mean that the absolute quantity of adsorbed SDS is increased. Above the plateau onset, some variation of the surface composition is observed at high surfactant concentration for the 0.5/0.5 mixture. However, the most important surface composition changes are observed in the case of the SDS-rich (0.3/0.7) mixture, although the same trends were already visible for the 0.5/0.5 system. Comparison between the profiles of the isotherms of Figures 2 or 3 with those of Figures 5−7 indicates that the surface composition changes occur in the same concentration region where the desorption of the surfactants is observed at higher concentrations as indicated by the second arrow. The complicated surface composition change may be due to the fact that the various oligomers of the polydispersed nonionic component do not desorb at the same rate as the total concentration is increased in the plateau region, depending upon the hydrophilic−lipophilic balance (HLB) (the nonpolar/polar molar mass ratio) of each oligomer. A thorough investigation of the adsorption/desorption behavior of each oligomer at the silica/water interface would be necessary in order
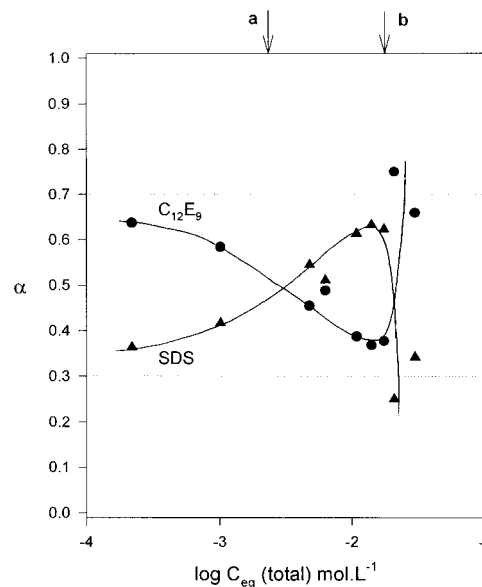
to interpret the global surface composition variation observed. That study was beyond the main purpose of the present work.

Conclusion

This investigation has confirmed previous studies which have shown that an ionic surfactant (SDS) which does not adsorb at a solid/water interface (silica/water) may be incorporated at that interface provided a second surfactant ($C_{12}E_9$) which adsorbs readily at that interface and forms mixed aggregates with the first component is added to the system. However, we have demonstrated that in the case where the first component is of the same electrical charge as the solid surface, both surfactants will eventually be desorbed from the interface at high surfactant concentration. This effect may be viewed as the consequence of the formation of free mixed micelles in the aqueous solution above the cmc which will be favored over the adsorbed mixed aggregates. The former case may be looked upon as a binary system with no strong repulsion forces between the two components whereas the latter case is a ternary system where the dissociated silanol surface groups induce the repulsion forces which eventually will lead to the surfactant desorption. The threshold concentration above which the desorption occurs depends on the initial binary surfactant composition. As expected, it occurs at lower concentrations as the surfactant (SDS) concentration is increased.