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Interactions in Mixed Micellar Systems of an Amphoteric Chelating Surfactant and Ionic Surfactants

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ABSTRACT: Mixtures of ionic surfactants and the chelating surfactant 2-dodecyldiethylenetriaminepentaacetic acid (4-C_{12}-DTPA) have been examined in terms of interactions in mixed micellar systems. The amphoteric 4-C_{12}-DTPA is zwitterionic with a negative net charge at the studied pH levels. The investigated ionic surfactants were the cationic dodecyltrimethylammonium chloride (DoTAC), the anionic sodium dodecyl sulfate (SDS), and the zwitterionic dimethyldodecylamine-*N*-oxide (DDAO). The surfactants all have the same hydrophobic chain lengths, and the results are evaluated in terms of headgroup interactions. 4-C_{12}-DTPA interacts with different ionic surfactants by accepting or donating protons to the aqueous solution to increase the attractive interactions between the two surfactants; i.e., the protonation equilibrium of 4-C_{12}-DTPA is shifted in different directions depending on whether there are predominant repulsions between positively or negatively charged groups in the mixed micelles. This was monitored by measuring pH vs concentration in the mixed systems. By measuring the pH, it was also possible to study the shift in the protonation equilibrium at increasing concentration, as the composition in the micelles approaches the composition in the total solution. Following the approach of Rubingh's regular solution theory, the interaction parameter β for mixed micelle formation was calculated from the cmc values determined by NMR diffusometry. Synergism in mixed micelle formation and negative β parameters were found in all of the investigated systems. As expected, the most negative β parameter was found in the mixture with DoTAC, followed by DDAO and SDS. The self-diffusion in the 4-C_{12}-DTPA/DoTAC system was also discussed. The self-diffusion coefficient vs concentration plots show two distinctly different curves, depending on the surfactant that is present in excess.
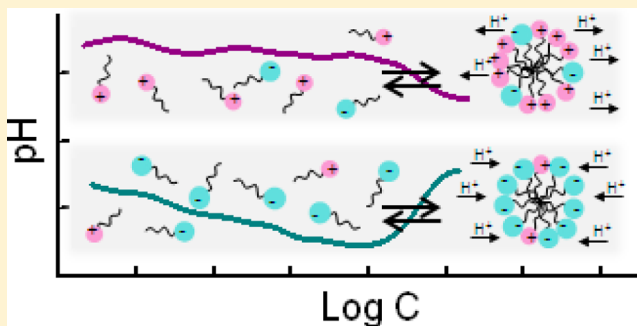
1. INTRODUCTION

In mixtures of two or more surfactants, synergism often appears due to favorable interactions between the different surfactants. This may result in reduced surface tension or critical micelle concentration for the mixed system. Surfactant mixtures are used in many practical applications due to the improved properties of the mixture compared to those of the individual surfactants. To obtain a measure of the interactions, the β parameter for mixed micelle formation in solutions is commonly calculated using the regular solution approach.[1] The calculated β parameter reflects the nature of the interactions in the mixture compared to the interactions between surfactants of the same kind. Although there are some limitations in this approximation, it provides a robust description of the nonideal behavior of surfactant mixtures. Investigations of the limiting assumption of zero entropy of mixing can be found in the literature; see for example Bergström and Eriksson.[2] Amphoteric surfactants, like the studied 4-C_{12}-DTPA,[3] can interact strongly with other ionic surfactants by accepting or donating protons to the aqueous solution in order to adjust the electrical charge and increase the attractive interactions.[4]

Chelating surfactants can be used to remove metal ions from aqueous solutions by for example foam flotation.[5] In such an application, a second surfactant may have to be added to improve the foaming, and the interactions between the two surfactants would play an important role in the efficiency of the process.[6−9] The studied chelating surfactant 4-C_{12}-DTPA has proved to be efficient for recovery of Cu^{2+} and Mn^{2+} ions by foam flotation in the presence of a foaming cosurfactant.[10−13]

In this paper we study the interactions in mixed micellar systems of 4-C_{12}-DTPA and three different ionic surfactants: the cationic DoTAC, the anionic SDS, and the zwitterionic DDAO. The interaction parameters β for the different mixtures are calculated from the cmc's determined by NMR diffusometry. The deviation from ideal mixing and the existence of synergism is investigated. The surfactants all have the same hydrocarbon chain length, and the effects are therefore discussed in terms of headgroup interactions.[14] The amphoteric nature of 4-C_{12}-DTPA is expected to contribute to increased attractive interactions in the studied mixed systems. The change in the protonation equilibrium of 4-C_{12}-DTPA, at the formation of mixed micelles, is therefore investigated by measuring the pH of the bulk solution as a function of total surfactant concentration. Finally, we discuss the plots of the self-diffusion

coefficient vs concentration at different mixing ratio in the 4-C_{12}-DTPA/DoTAC system.

2. EXPERIMENTAL SECTION

2.1. Materials. The chelating surfactant 2-dodecyldiethylenetriaminepentaacetic acid (4-C_{12}-DTPA) was delivered by Syntagon AB. The synthesis and analyses have been reported earlier.[3,15] Water for preparation of samples was of Milli-Q grade. Dodecyltrimethylammonium chloride (DoTAC), sodium dodecyl sulfate (SDS), and dimethyldodecylamine-N-oxide (DDAO) were of analytical grade and used without further purification.

2.3. Sample Preparation. Concentrated stock solutions of the different surfactants and mixtures were prepared at different pH by appropriate amounts of surfactant(s) and sodium hydroxide or hydrochloric acid in water. The pH given in the text refers to the pH of the stock solutions. All samples for pH, surface tension, and NMR diffusometry measurements were prepared by diluting concentrated stock solutions with pH adjusted water. The samples were kept in sealed bottles after preparation.

2.5. Surface Tension Measurements. The surface tension was measured with a Krüss K6 tensiometer and a platinum du Noüy ring at a temperature of approximately 22 °C. The surface tension was measured once right after sample preparation, and then the sample was left for 5 min before it was measured four times consecutive. The mean values are reported. Where applicable, the critical micelle concentration was determined at the concentration where the surface tension begins to increase again, in accordance with our previous conclusions.[3]

2.6. pH. pH was measured at a temperature of approximately 22 °C using a Mettler Inlab micro pH electrode.

2.7. NMR Diffusometry. The NMR diffusometry measurements were carried out using the stimulated echo pulsed field gradient (STE-PFG) NMR sequence. This technique is well established, and a detailed description can be found elsewhere.[16−18] The NMR experiments were performed on a Bruker Avance DPX 250 MHz NMR spectrometer equipped with a standard Bruker self-diffusion probe. The temperature was kept at 26 °C. The attenuation of the echo signal was fitted using eq 1 to extract the self-diffusion coefficient D:

$$I = I_0 e^{\{-D(2\pi\gamma G\delta)^2(\Delta - \delta/3)\cdot 10^4\}} \tag{1}$$

where I denotes the observed echo intensity, I_0 is the echo intensity in the absence of field gradient pulses, γ is the magnetogyric ratio, G is the field gradient strength, δ is the duration of the gradient pulse, and Δ is the time between the leading edges of the gradient pulses. In all experiments δ was set to 1.5 ms and Δ to 40 ms while the gradient G was varied linearly. For the water self-diffusion measurements we used a repetition time of 10 000 ms, gradient starting value of 5 G/cm, end value 75 G/cm, and 21 data points were measured, while for the surfactant measurements we used a repetition time of 3000 ms, gradient starting value of 75 G/cm to suppress the water signal as much as possible without compromising the surfactant signals, end value adjusted to the expected self-diffusion coefficient for the surfactant, and at least 31 data points were measured. The cmc's are determined from the self-diffusion coefficient vs concentration plots.

3. RESULTS AND DISCUSSION

3.1. Interaction Parameter and Synergism in Mixed Micelles. The molecular structure of the chelating surfactant 4-C_{12}-DTPA, with eight donor atoms that can coordinate metal ions, is shown in Figure 1. In the absence of metal ions, the donor atoms are titrating and the charge of the headgroup depends on the dissociation of the functional groups. Theoretically, the headgroup charge can vary from +3 at low pH to −5 at high pH. Over a large pH interval, including the studied pH levels of 5 and 7, 4-C_{12}-DTPA is zwitterionic with a negative net charge, which increases with increasing pH.
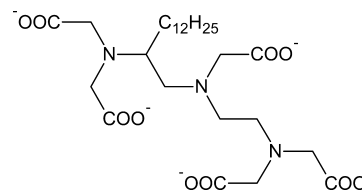

Figure 1. Molecular structure of 4-C_{12}-DTPA at high pH, with eight titrating groups, i.e., the five carboxylate groups and the three tertiary amine groups.

4-C_{12}-DTPA was examined in mixtures with three different ionic surfactants; the cationic DoTAC, the anionic SDS, and the zwitterionic DDAO. We have earlier reported that the surface tension vs concentration plot of 4-C_{12}-DTPA exhibits unconventional behavior in that the surface tension reaches a plateau due to saturation of the surface at a concentration significantly lower than the cmc (which was determined by NMR diffusometry) and that the surface tension increases with the concentration above the cmc due to surfactants favoring the micelles over the saturated surface once the cmc was reached (see Figure 2a).[3] In the mixtures studied here, this behavior
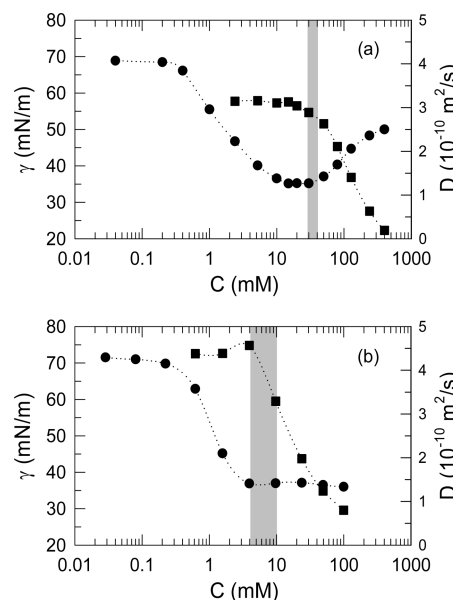

Figure 2. Correlations between NMR diffusometry (■) and surface tension (●) vs concentration for (a) 4-C_{12}-DTPA and (b) 4-C_{12}-DTPA/SDS at $\alpha_{4\text{-C12-DTPA}} = 0.25$. The determined cmc's are highlighted by the gray zones.

becomes less pronounced with decreasing mole fraction of 4-C_{12}-DTPA and finally extinguishes in the mixtures with SDS or DoTAC as the mole fraction of 4-C_{12}-DTPA is reduced to 0.25. Note the difference between the surface tension plot in Figure 2a for the pure 4-C_{12}-DTPA and in Figure 2b for the 4-C_{12}-DTPA/SDS mixture at $\alpha_{4\text{-C12-DTPA}} = 0.25$. This can be explained when considering the geometry of the surfactants. The critical packing parameter, cpp, which is the ratio between the cross-sectional area of the hydrophobic and the hydrophilic parts, is useful in this context. For ionic surfactants, like SDS and DoTAC, cpp ≤ 1/3 is usually found. We can state, even without determining the headgroup area, that 4-C_{12}-DTPA must have a cpp significantly lower than SDS and DoTAC due to its large headgroup. The size of the headgroup is most likely

Table 1. Experimentally Determined cmc's of the Individual Surfactants and Their Mixtures and Average Calculated β Parameter for Mixed Micelle Formation

surfactant 1/surfactant 2	pH	type[a]	cmc_1[b] (mM)	cmc_2 (mM)	$|\ln(cmc_1/cmc_2)|$	$cmc_{12,min}$[c] (mM)	β[d]
4-C$_{12}$-DTPA/DoTAC	5	Z/C	20 ± 3	20 ± 5	0	2 ± 0.5	−9.3
4-C$_{12}$-DTPA/DDAO	7	Z/Z	35 ± 10	3 ± 1	2.5	2 ± 0.3	−6.2
4-C$_{12}$-DTPA/SDS	5	Z/A	20 ± 3	9 ± 3	0.8	6 ± 2	−3.1
4-C$_{12}$-DTPA/SDS	7	Z/A	35 ± 10	9 ± 3	1.4	7 ± 3	−3.6

[a]Z = zwitterionic, C = cationic, A = anionic. [b]From ref 3. [c]At the point of maximum synergism. [d]Average of the calculated β parameters at the different mixing ratios.

the reason why 4-C$_{12}$-DTPA saturates the surface at a concentration lower than the cmc, and with its low cpp, 4-C$_{12}$-DTPA is geometrically more suited in micelles than at the air−water interface and consequently favors the micelles once the cmc is reached. Conventional behavior is attained when SDS or DoTAC is present in excess due to the smaller headgroups and larger cpp of these surfactants (see Figure 2b). The surface does not necessarily reach saturation,[19] or it becomes saturated approximately at the cmc, and consequently the break in the surface tension plot is consistent with the cmc determined from NMR diffusometry. Furthermore, there is no significant change in the surface tension above the cmc.

The interaction parameter β for mixed micelle formation was calculated using Rubingh's regular solution theory.[1] The critical micelle concentration of a mixture of two surfactants, cmc_{12}, at the mole fraction α of surfactant 1 (on a surfactant-only basis) can be calculated from the cmc's of the individual surfactants 1 and 2 (cmc_1 and cmc_2) and the activity coefficients of surfactants 1 and 2 in the mixed micelle (f_1^M and f_2^M).

$$\frac{1}{cmc_{12}} = \frac{\alpha}{f_1^M cmc_1} + \frac{1-\alpha}{f_2^M cmc_2} \quad (2)$$

When there is no net interaction between the two surfactants, i.e., in the ideal case, $f_1^M = f_2^M = 1$. In the nonideal case, the activity coefficients of the surfactants in the mixed micelle can be calculated from the regular solution theory.

$$\ln f_1^M = (1 - X_1^M)^2\beta \quad \text{and} \quad \ln f_2^M = (X_1^M)^2\beta \quad (3)$$

X_1^M is the mole fraction of surfactant 1 (on a surfactant-only basis) in the micelles, and β is calculated from the cmc's of the individual surfactants and their mixture at α. Equation 4 is solved numerically for X_1^M, which is then substituted into eq 5 to calculate β. Here, the cmc's were determined by NMR diffusometry if not otherwise stated.

$$\frac{(X_1^M)^2 \ln(\alpha cmc_{12}/X_1^M cmc_1)}{(1-X_1^M)^2 \ln[(1-\alpha)cmc_{12}/(1-X_1^M)cmc_2]} = 1 \quad (4)$$

$$\beta = \frac{\ln(\alpha cmc_{12}/X_1^M cmc_1)}{(1-X_1^M)^2} \quad (5)$$

It should be noted that the numerous titrating groups with overlapping pK_a values of 4-C$_{12}$-DTPA complicate the description of the systems. In a solution of 4-C$_{12}$-DTPA at any intermediate pH level, there will be a distribution of differently charged species present rather than a single 4-C$_{12}$-DTPA surfactant with a defined charge. The distribution of the different species is governed by the pK_a values, and the complexity in the system depends on the number of overlapping pK_a values at the specific pH. This picture becomes even more complex as micelles start to form, since the high

charge density at the micellar surface affects the dissociation of surfactants in micelles.[3] A solution of 4-C$_{12}$-DTPA is thus already a mixed system, where the different components and mixing ratio depend on the pH. Because of this, it may seem questionable to treat the studied mixtures of 4-C$_{12}$-DTPA and a second surfactant as a binary mixture. However, provided the awareness of these limitations, we find the calculation of the β parameter useful for the understanding of the interactions in mixtures containing an amphoteric surfactant. The following limitations are assumed: (i) the pure 4-C$_{12}$-DTPA is defined as the distribution of differently charged species at the specific pH, (ii) the dissociation of 4-C$_{12}$-DTPA surfactants in the mixed micelles will be affected by the presence of the second surfactant and thus may the mixed micelles consist of a distribution of 4-C$_{12}$-DTPA species that differs from the distribution in the pure 4-C$_{12}$-DTPA micelles, and (iii) the interaction parameter is dominated by the strongest interactions in the systems, and the calculated β parameter primarily describes these interactions.

The β parameter reflects the nature of the interactions in the mixed system relative to the self-interactions for the two individual surfactants. The value of β is proportional to the free energy of mixing, and the stronger the attractions and/or the weaker the repulsions in the mixture relative to the self-interactions for the individual surfactants, the more negative is the β parameter. Here, surfactants with the same hydrophobic chain length were studied, so the effects are related to interactions between headgroups. When the cmc of a mixture of two surfactants is lower than the cmc of either individual surfactant, the system exhibits synergism in mixed micelle formation. The two conditions for this type of synergism to occur is (i) the β parameter must be negative and (ii) $|\beta| > |\ln(cmc_1/cmc_2)|$.[20] The maximum synergism and minimum cmc of a mixture ($cmc_{12,min}$) are found at the point where $\alpha = X_1^M$, i.e., when the composition of the solution equals the optimum composition in the mixed micelles. The average value of the interaction parameters calculated from eqs 4 and 5 as well as the minimum cmc's of the investigated mixtures are shown in Table 1. In a solution containing only 4-C$_{12}$-DTPA, we can assume that the factors opposing micellization are steric repulsions between the bulky headgroups as well as electrostatic repulsions due to the negative net charge. For the cationic DoTAC, there are strong electrostatic self-repulsions between the positively charged headgroups. As shown in Table 1, mixing these two surfactants results in a synergistic reduction of the cmc and a large negative β parameter due to the element of attractive interactions between their oppositely charged headgroups. The amphoteric 4-C$_{12}$-DTPA interacts with different surfactants by accepting or donating protons to the aqueous solution in order to increase the attractive interactions between the two surfactants. The increased protonation increases the relative amount of positive charges, whereas the donation of
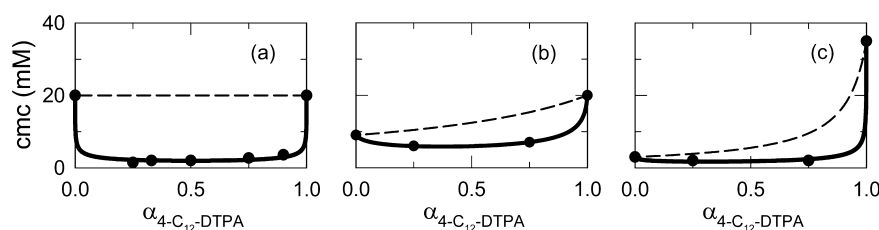
Figure 3. Experimentally determined (●), calculated ideal case (− − −) and calculated nonideal case (—) cmc vs mole fraction of 4-C_{12}-DTPA for (a) 4-C_{12}-DTPA/DoTAC at pH 5, $\beta = -9.3$, (b) 4-C_{12}-DTPA/SDS at pH 5, $\beta = -3.1$, and (c) 4-C_{12}-DTPA/DDAO at pH 7, $\beta = -6.2$.

protons increases the relative amount of negative charges. The increased dissociation of 4-C_{12}-DTPA in the presence of the cationic DoTAC, which will be further discussed in section 3.2, contributes to the attractive interactions between the two surfactants.

The 4-C_{12}-DTPA/DDAO mixture was examined at pH 7, where DDAO is a zwitterionic surfactant capable of accepting a proton from the aqueous solution and become cationic. The pK_a value of DDAO monomers is 4.78.[21] In this system, both surfactants can adjust to the interactions in the mixed micelles by accepting protons. As shown in Table 1, the cmc$_{12,min}$ of the 4-C_{12}-DTPA/DDAO and the 4-C_{12}-DTPA/DoTAC mixtures are the same, meaning that micelles are formed just as easily in both systems. Even though there are clearly attractive interactions between the two zwitterionic surfactants, the β parameter for the mixture with DDAO indicates less deviation from ideal behavior than in the mixture with DoTAC. This is probably a combined effect of the much weaker self-repulsions of DDAO compared to DoTAC and the large difference between the cmc's of 4-C_{12}-DTPA and DDAO. Less deviation from ideal behavior is usually observed the more the cmc's of the individual surfactants differ.

Negative β values and synergism in mixed micelle formation were found also in the 4-C_{12}-DTPA/SDS mixtures but of smaller magnitude due to repulsion between 4-C_{12}-DTPA and the anionic SDS. The interaction with the anionic SDS increases the protonation of 4-C_{12}-DTPA in order to reduce its negative net charge. The synergism may be due to screening of the self-repulsions, especially the steric self-repulsions for 4-C_{12}-DTPA surfactants, as well as attractive interactions between the negatively charged SDS surfactants and the positive charges on the protonated amine groups in the zwitterionic 4-C_{12}-DTPA. The β value of the 4-C_{12}-DTPA/SDS mixture was only slightly affected by the increase in pH from 5 to 7, and the effect may seem contradictory at first. Even though the increased negative net charge of 4-C_{12}-DTPA at pH 7 is expected to increase the repulsion between SDS and 4-C_{12}-DTPA in the mixed micelles, the β parameter is in fact slightly more negative at this higher pH. This must be because the increased self-repulsion of 4-C_{12}-DTPA at pH 7 has a larger effect on the interaction parameter.

The experimentally determined cmc vs surfactant composition in the solution is shown in Figure 3 for the mixtures with DoTAC and SDS at pH 5 and DDAO at pH 7. The cmc's at $\alpha_{4\text{-}C12\text{-}DTPA} = 0.75$ and 0.9 in the mixture with DoTAC were determined from surface tension measurements due to difficulties in determining these from NMR diffusometry (see section 3.3). The relationship calculated from eq 2 for the ideal case, when there is no net interaction between the surfactants ($\beta = 0$), as well as for the nonideal case with the average β parameters given in Table 1 is also shown in Figure 4. 4-C_{12}-DTPA/DoTAC is the system that deviates most from ideal
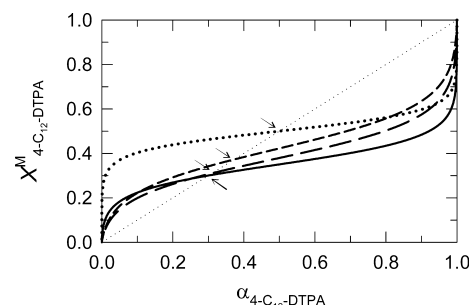

Figure 4. Mole fraction of 4-C_{12}-DTPA in micelles vs mole fraction of 4-C_{12}-DTPA in solution for 4-C_{12}-DTPA/DoTAC at pH 5 (···), 4-C_{12}-DTPA/SDS at pH 5 (- - -), 4-C_{12}-DTPA/SDS at pH 7 (− − −), and 4-C_{12}-DTPA/DDAO at pH 7 (—). The different optimum compositions for the mixtures are indicated by the arrows.

mixing over the whole solution composition because of the large negative β value and the similar cmc's of the individual surfactants. When there is a large difference in the cmc's of the individual surfactants, as in the 4-C_{12}-DTPA/DDAO mixture, the ideal mixing predicts a large deviation from a straight line in the cmc's of the mixtures due to a larger fraction of the surfactant with the lower cmc in the mixed micelles, in this case DDAO. Consequently, there is not that much difference between the ideal case and the nonideal case at low mole fraction of 4-C_{12}-DTPA.

The micellar composition at cmc vs the solution composition is shown for all four mixtures in Figure 4. The maximum synergism and minimum cmc are found at the point where the solution composition equals the optimum composition in the mixed micelles, i.e., where the curves in the figure cross the diagonal. For two surfactants with similar cmc values, as in the 4-C_{12}-DTPA/DoTAC mixture, the optimum composition is 0.5. The β parameter is visible in the slope of the linear part of the curve; the stronger the attraction between the two surfactants, the stronger is the tendency of the system to strive toward the optimum composition in micelles over the whole solution composition. When the cmc values differ, the optimum composition is shifted toward increased mole fraction of the surfactant with the lowest cmc, as in the mixture with DDAO. The effect of increasing the pH from 5 to 7, which increases the cmc of 4-C_{12}-DTPA, is visible in the 4-C_{12}-DTPA/SDS system. The optimum composition is shifted toward decreased mole fraction of 4-C_{12}-DTPA as the pH is increased.

3.2. Effects of Mixed Micelle Formation on pH. The effect of interactions in micelles containing 4-C_{12}-DTPA can be seen also on the pH of the solution due to the possibility of 4-C_{12}-DTPA to accept or donate protons to the aqueous solution in order to adjust its electrical charge. The increased charge density at the micellar surface affects the dissociation of the aggregated surfactants compared to the free monomers, and the

effect on the pH is shown in Figure 5 for the 4-C$_{12}$-DTPA/ DoTAC system. The initial pH of the mixtures shown in the
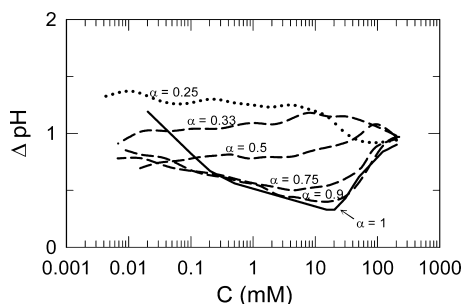

Figure 5. ΔpH vs total surfactant concentration for 4-C$_{12}$-DTPA/ DoTAC mixtures at $\alpha_{\text{4-C12-DTPA}}$ between 0.25 and 1, initial pH around 5.

figure differed slightly, and the pH axis has therefore been shifted for some of the curves, maximum 0.4 pH units, for clarification. In the pure 4-C$_{12}$-DTPA solution ($\alpha_{\text{4-C12-DTPA}}$ = 1), surfactants in micelles are protonated to a higher degree to screen the electrostatic repulsions between adjacent negatively charged surfactants, which is evident from the increasing pH of the solution at the formation of micelles. Adding the cationic DoTAC changes the electrostatic environment in the micelles, as seen from the change in the shape of the curves with the surfactant composition in Figure 5. When the mixtures are rich in 4-C$_{12}$-DTPA, the behavior is similar to the pure 4-C$_{12}$-DTPA solution, meaning that there are still repulsions between the negative charges on 4-C$_{12}$-DTPA since the pH increases at the cmc. At increasing mole fraction of DoTAC, the pH curves levels off as the amount of positive charges approaches the amount of negative charges in the mixture, and the need for neutralization of electrostatic repulsions decreases. At $\alpha_{\text{4-C12-DTPA}}$ = 0.33 there are rather small variations in pH, but the shape of the curve differs distinctly from the mixtures at high mole fraction of 4-C$_{12}$-DTPA, which is an indication that the mixing ratio in the total solution has passed the point of electroneutrality. The surfactant composition in micelles at the cmc differs from the composition in the solution, as shown in Figure 4. At increasing concentration, however, the composition in the micelles must approach the composition in the total system as the monomer concentration becomes negligible. Because of this change in mixing ratio of the two types of surfactants in the micelles, the pH curve will never become perfectly flat over the examined concentration interval. At $\alpha_{\text{4-C12-DTPA}}$ = 0.33, the mole fraction of 4-C$_{12}$-DTPA in micelles is around 0.47 at the cmc (see Figure 4), and the pH increases at the formation of micelles due to the repulsions between 4-C$_{12}$-DTPA. As the concentration increases and the mixing ratio in the micelles approaches that of the total system ($\alpha_{\text{4-C12-DTPA}}$ = 0.33), the pH start to decrease at the point where the repulsions between DoTAC starts to dominate. This is because of the increased dissociation of 4-C$_{12}$-DTPA to increase the amount of negative charges in the micelles. At the highest mole fraction of DoTAC ($\alpha_{\text{4-C12-DTPA}}$ = 0.25), the mole fraction of 4-C$_{12}$-DTPA in micelles is around 0.45 at the cmc, and now the pH remains constant at the formation of micelles, indicating equal amounts of positive and negative charges in the micelles. The pH drops at higher concentrations when the molar ratio of DoTAC in the micelles increases as the composition in the micelles approaches the total composition.

For the mixtures with SDS and DDAO, the pH behavior is similar at all mixing ratios. As shown in Figure 6, the presence
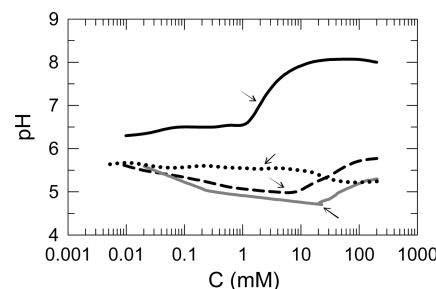

Figure 6. pH vs total surfactant concentration at $\alpha_{\text{4-C12-DTPA}}$ = 0.25 for 4-C$_{12}$-DTPA/DDAO (—), 4-C$_{12}$-DTPA/DoTAC (···), and 4-C$_{12}$-DTPA/SDS (- - -) as well as for the pure 4-C$_{12}$-DTPA (gray line). The arrows indicate the cmc values determined by NMR diffusometry.

of the anionic SDS surfactants in the 4-C$_{12}$-DTPA/SDS mixtures results in a similar pH behavior as for the pure 4-C$_{12}$-DTPA solution, since the increased protonation of 4-C$_{12}$-DTPA reduces the repulsions in the mixed micelles. In the 4-C$_{12}$-DTPA/DDAO mixtures, the effect on pH is enhanced due to the simultaneous titration of DDAO surfactants. The zwitterionic DDAO can accept a proton from the aqueous solution and become cationic. By the increased protonation of both types of surfactants in the mixed micelles, the negative net charge of 4-C$_{12}$-DTPA is reduced at the same time as the positive charge on DDAO increases. The mixture with DoTAC, from Figure 6, is shown for comparison.

3.3. NMR Diffusometry in the 4-C$_{12}$-DTPA/DoTAC System.
NMR diffusometry measurements were performed on the mixed systems in order to determine the cmc's. When plotting the self-diffusion coefficient vs concentration, two types of curves revealed. Although a complete analysis of the self-diffusion in the systems lies beyond the scope of this article, we will discuss possible causes of the two types of curves. It is clear that the type of curve depends on the surfactant that is present in excess, indicating that the behavior is connected to the interactions in the system. The self-diffusion coefficient vs concentration is shown in Figure 7 for the 4-C$_{12}$-DTPA/
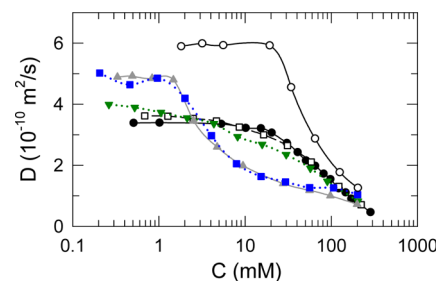

Figure 7. Self-diffusion coefficient vs concentration for 4-C$_{12}$-DTPA/ DoTAC mixtures at $\alpha_{\text{4-C12-DTPA}}$ = 0 (○), $\alpha_{\text{4-C12-DTPA}}$ = 0.25 (■), $\alpha_{\text{4-C12-DTPA}}$ = 0.5 (▲), $\alpha_{\text{4-C12-DTPA}}$ = 0.75 (▼), $\alpha_{\text{4-C12-DTPA}}$ = 0.9 (□), and $\alpha_{\text{4-C12-DTPA}}$ = 1 (●).

DoTAC mixtures at different surfactant compositions. For the pure DoTAC ($\alpha_{\text{4-C12-DTPA}}$ = 0), the self-diffusion coefficient is approximately constant at concentrations up to cmc, where there is a sharp break after which the self-diffusion drops significantly due to the formation of micelles. The two mixtures at high mole fraction of DoTAC ($\alpha_{\text{4-C12-DTPA}}$ from 0.25 to 0.5)

resemble the pure DoTAC with well-defined cmc's, i.e., sharp breaks. These two curves are practically overlapping, meaning that the variation in molar composition from $\alpha_{4\text{-C12-DTPA}} = 0.25$ to 0.5 affect neither monomers nor micelles to any great extent. The fluctuations in the curves at low concentrations are most probably due to long experimental times. We would however have expected the monomer self-diffusion to gradually decrease as the mole fraction of 4-C_{12}-DTPA increases due to the slower self-diffusion coefficient of 4-C_{12}-DTPA compared to DoTAC at concentrations below the cmc.

The character of the self-diffusion vs concentration plot suddenly changes as the surfactant composition becomes dominated by 4-C_{12}-DTPA. At the highest mole fraction of 4-C_{12}-DTPA ($\alpha_{4\text{-C12-DTPA}} = 0.75$ and 0.9) the self-diffusion coefficient is slightly depending on the concentration already below the macroscopic cmc, particularly evident at $\alpha_{4\text{-C12-DTPA}} = 0.75$. Furthermore, the slope of the curve becomes progressively more negative, on the logarithmic scale, over a large concentration interval instead of the usually observed sharp break. A possible explanation to this may be that there are premicellar aggregates present in the solution.[22,23] The slightly declining self-diffusion coefficient at concentrations below cmc may be due to an increasing contribution from premicellar aggregates at the expense of free monomers.[24] However, given the large headgroup of 4-C_{12}-DTPA, and since DoTAC is known to form spherical micelles easily, this seems somewhat contradictory. Instead of the usual steep drop at the cmc, there is a smooth transition toward the micellar self-diffusion. Without further analyses, we can only speculate about the cause of this concentration dependence. Since the measured self-diffusion coefficient is a population average of the different states, the smooth transition may be related to a distribution in the size of the aggregates, possibly in turn related to the distribution of differently charged 4-C_{12}-DTPA species. In a study by Cui et al. the curved dependence of the self-diffusion coefficient vs concentration was explained by smaller aggregates growing into the size of the micelles as the concentration increased.[25] At sufficiently high concentration, the slope of the curve eventually begins to level off toward the micellar self-diffusion.

The two types of curves of the mixed systems are tending toward different micellar self-diffusion coefficients at higher concentrations, probably due to different form factors of the micelles. At higher concentrations, the micelles may also be affected by obstruction.

4. CONCLUSIONS

Mixtures of ionic surfactants and the chelating surfactant 4-C_{12}-DTPA were examined in terms of headgroup interactions in mixed micellar systems. 4-C_{12}-DTPA is an amphoteric surfactant with a large headgroup containing numerous titrating groups, capable of both accepting and donating protons to the aqueous solution to form a number of differently charged species. The distribution of species depends not only on the pH but also on the state of the surfactants since the higher charge density at the micellar surface affects the dissociation of the aggregated surfactants. The described systems containing 4-C_{12}-DTPA are therefore rather complex mixtures. At the investigated pH levels, the most abundant species of 4-C_{12}-DTPA are zwitterionic with negative net charge. The presence of a second surfactant shifts the protonation equilibrium of 4-C_{12}-DTPA in the direction of increased attractive interaction in the mixed micelles. The amphoteric nature of 4-C_{12}-DTPA

contributes thereby to enhanced attractive interactions in the mixed micelles by increasing or decreasing its degree of protonation in order to reduce the electrostatic repulsions.

We have demonstrated that the simple technique of measuring the pH of the surrounding solution as a function of concentration gives valuable information in mixed systems containing an amphoteric surfactant. The shift in the protonation equilibrium of 4-C_{12}-DTPA at the formation of micelles is visible in the pH change of the solution. Interactions with anionic and cationic surfactants affect the protonation equilibrium in different directions. Increasing pH was observed as a result of increased protonation of 4-C_{12}-DTPA to screen the electrostatic repulsions between negatively charged groups. In the case of repulsions between positively charged groups, on the other hand, the pH of the solution decreased due to release of protons from 4-C_{12}-DTPA at the formation of micelles. The pH measurements are particularly informative in a system such as the 4-C_{12}-DTPA/DoTAC, where there is repulsion between negatively charged groups at high mole fraction of 4-C_{12}-DTPA and between positively charged groups at high mole fraction of DoTAC. In this system, we can also see that the composition in micelles changes with the concentration, as predicted by Rubing's regular solution theory. As the concentration increases, the composition in the micelles approaches the composition in the total solution.

As expected, given the amphoteric nature of 4-C_{12}-DTPA, synergism in mixed micelle formation and negative β parameters were found in all of the investigated systems. Because of the negative net charge of 4-C_{12}-DTPA, the most negative β parameter was found in the mixture with the cationic DoTAC. When plotting the self-diffusion constant vs the concentration at different mole fractions of 4-C_{12}-DTPA, two distinctly different curves appeared. The results were interpreted as indication of premicellar aggregation at high mole fraction of 4-C_{12}-DTPA.

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Notes
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