

Mixed Micellization of Dimeric (Gemini) Surfactants and Conventional Surfactants

II. CMC and Micelle Aggregation Numbers for Various Mixtures

R. G. Alargova,^{*,†,1} I. I. Kochijashky,^{*} M. L. Sierra,[§] K. Kwetkat,[‡] and R. Zana^{§,2}

^{*}Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, University of Sofia, Sofia, Bulgaria; [†]The DEEPSTAR Group, Japan Marine Science and Technology Center, 2-15 Natsushima-cho, Yokosuka-shi 2370061, Japan; [‡]Condea, Chemicals GmbH, P. Baumann Strasse, gebäude 1162/PB14, 45764, Marl, Germany; and [§]Institut Charles Sadron (CNRS-ULP), 6 rue Boussingault, 67000 Strasbourg, France

Received May 16, 2000; accepted October 30, 2000

The aqueous solutions of mixtures of various conventional surfactants and dimeric anionic and cationic surfactants have been investigated by electrical conductivity, spectrofluorometry, and time-resolved fluorescence quenching to determine the critical micelle concentrations and the micelle aggregation numbers in these mixtures. The following systems have been investigated: 12-2-12/DTAB, 12-2-12/ $C_{12}E_6$, 12-2-12/ $C_{12}E_8$, 12-3-12/ $C_{12}E_8$, Dim3/ $C_{12}E_8$, and Dim4/ $C_{12}E_8$ (12-2-12 and 12-3-12 = dimethylene-1,2- and trimethylene-1,3-bis(dodecyltrimethylammonium bromide), respectively; $C_{12}E_6$ and $C_{12}E_8$ = hexa- and octaethyleneglycol monododecylethers, respectively; Dim3 and Dim4 = anionic dimeric surfactants of the disodium sulfonate type, Scheme 1; DTAB = dodecyltrimethylammonium bromide). For the sake of comparison the conventional surfactant mixtures DTAB/ $C_{12}E_8$ and SDS/ $C_{12}E_8$ (SDS = sodium dodecylsulfate) have also been investigated (reference systems). Synergism in micelle formation (presence of a minimum in the cmc vs composition plot) has been observed for the Dim4/ $C_{12}E_8$ mixture but not for other dimeric surfactant/nonionic surfactant mixtures investigated. The aggregation numbers of the mixed reference systems DTAB/ $C_{12}E_8$ and SDS/ $C_{12}E_8$ vary monotonously with composition from the value of the aggregation number of the pure $C_{12}E_8$ to that of the pure ionic component. In contrast, the aggregation number of the dimeric surfactant/ $C_{12}E_8$ mixtures goes through a minimum at a low value of the dimeric surfactant mole fraction. This minimum does not appear to be correlated to the existence of synergism in micelle formation. The initial decrease of the aggregation number of the nonionic surfactant upon addition of ionic surfactant, up to a mole fraction of ionic surfactant of about 0.2 (in equivalent per total equivalent), depends little on the nature the surfactant, whether conventional or dimeric. The results also show that the microviscosity of the systems containing dimeric surfactants is larger than that of the reference systems.

© 2001 Academic Press

Key Words: mixed micellization; dimeric surfactant/conventional surfactant mixtures; cmc of surfactant mixtures; mixed micelle aggregation numbers; time-resolved fluorescence quenching.

INTRODUCTION

Dimeric (gemini) surfactants are attracting considerable interest in both academic and industrial research laboratories owing to their low cmc values and their stronger efficacy in decreasing the surface tension of water (lower p_{20} values) than the corresponding conventional surfactants (1–3). These surfactants are expected to be commercially used in the near future, probably as specialist surfactants. The German company Condea is already proposing formulations based on anionic dimeric surfactants. Since most formulations generally use complex mixtures of different surfactants, anionic, nonionic, and eventually cationic, we have undertaken a systematic study of mixed micellization in mixtures of conventional surfactants and dimeric surfactants in aqueous solution. The mixtures are characterized by their critical micellization concentration (cmc) and total micelle aggregation numbers (N_T , total number of surfactant chains per micelle) determined as a function of the mixture composition. In Part I in this series (4) we reported on the cmc and micelle aggregation number in mixtures of the nonionic surfactants $C_{12}E_5$ and $C_{12}E_8$ (penta- and octaethyleneglycol monododecylethers, respectively) and the anionic dimeric surfactant disodium 1,11-didecyl-3,6,9-trioxaundecane-1,11-disulfate (referred to as Dim1). Synergism in micelle formation was evidenced in these mixtures by the presence of a minimum in the cmc vs composition plot. The results for the micelle aggregation number of the mixtures showed a nonideal mixing behavior with a shallow minimum in the variation of N_T with the mixture composition at a Dim1 mole fraction around 0.5. Synergism in formation of micelles and monolayers by mixtures of nonionic conventional surfactants and anionic dimeric

¹ On leave from the University of Sofia and presently at the Japan Marine Science and Technology Center.

² To whom correspondence should be addressed.

surfactants has been investigated by Rosen *et al.* (5–7). The literature reports many measurements of micelle aggregation number in solutions of surfactant mixtures (8–24). Most of these measurements have been performed at a finite total surfactant concentration using fluorescence probing techniques (12–22, 24). Indeed, the variation of the mixed micelle aggregation number with both concentration and composition introduces difficulties in the interpretation of the results obtained using conventional methods of measurements, such as light scattering, or methods based on colligative properties (25). Measurements involving mixtures of conventional and dimeric surfactants are much less numerous (4, 11, 24).

The work described in Part I has been expanded by studying mixtures of several dimeric surfactants (both cationic and anionic) with conventional surfactants (ionic and nonionic). For the sake of comparison we have also investigated mixtures of nonionic conventional surfactants with ionic surfactants that can be considered as the monomers of the dimeric surfactants used. The cmc and micelle aggregation numbers in the mixtures have been systematically measured and are reported below.

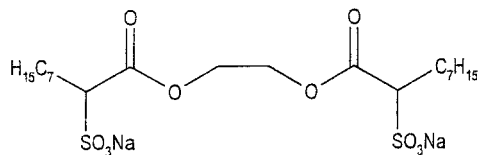
EXPERIMENTAL

Materials

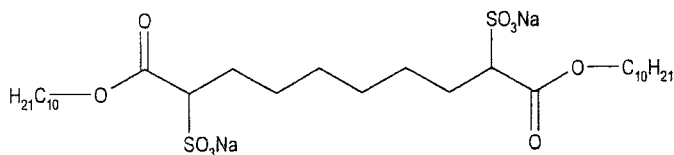
The surfactants used in this study are the conventional (monomeric) surfactants C₁₂E₆ (hexaethyleneglycol monododecylether, from Nikko, Japan; cmc = 0.12 mM (25)), C₁₂E₈ (octaethyleneglycol monododecylether, from Nikko, Japan; cmc = 0.08 mM (11)), DTAB (dodecyltrimethylammonium bromide, from Aldrich; cmc = 15 mM (26)), and SDS (sodium dodecylsulfate, from Touzart-Matignon, France; cmc = 8 mM (27)), and the cationic dimeric surfactants 12-2-12 (dimethylene-1,2-bis(dodecyldimethylammonium bromide), synthesized by us; cmc = 0.84 mM (27) and 12-3-12 (trimethylene-1,3-bis(dodecyldimethylammonium bromide), synthesized by us; cmc = 0.93 mM (28)) and two anionic dimeric surfactants referred to as Dim3 (cmc = 5.7 mM, this work) and Dim4 (cmc = 0.13 mM, this work), synthesized and purified as described below. The origin or synthesis and purification of the conventional and cationic dimeric surfactants are reported in the references given with each surfactant cmc (25–28).

The synthesis of the dimeric surfactant Dim3 (see chemical structure in Scheme 1) was realized in two steps. First, a 1/1 mixture of C₈ and C₁₀ fatty acid methylesters was reacted with a mixture of sulfur trioxide and air (7% vol/vol) at 45°C, in a glass falling film reactor (length 1.56 m, diameter 0.014 m). The reaction mixture (8 kg) was stirred for 30 min at 80°C. A ¹³C NMR analysis showed that 90 mol% of the resulting product was the required α-sulfo fatty acid methyl ester. The rest was identified as its sulfo ester, resulting from the insertion of sulfur trioxide into the ester bond. The second step consisted in a transesterification of the α-sulfo fatty acid methyl ester (1 mol) with ethylene glycol (1 mol). Upon the mixing of the reactants the temperature rose to 50°C, and it was further increased to 140°C. The reaction

Dim 3 (represented with the average alkyl chain length)

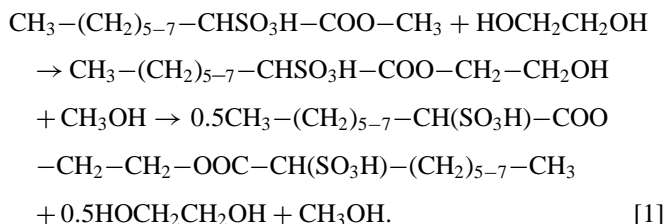


Dim 4



Scheme 1. Structure of the two anionic dimeric surfactants.

produces methanol and ethylene glycol, according to



The ethylene glycol and methanol were removed under vacuum. The resulting product was dark brown and highly viscous. It was neutralized with a 2 N sodium bicarbonate solution at 60°C, yielding the raw Dim3 surfactant, which was further purified by column chromatography, on Kieselgel 60 with ethylacetate/methanol (4/1 vol/vol) as solvent. The elemental analysis gave satisfactory results.

The Dim4 surfactant (disodium salt of di-α-sulfosebacinic acid di-decanol ester, see chemical structure in Scheme 1) was also synthesized in two steps. In the first step sebacinic acid dimethyl ester (5 kg) was reacted with a sulfur trioxide/air mixture (7% vol/vol) at 70°C, in a 10-liter batch reactor with cooling coils and a gas inlet. Once the addition of sulfur trioxide was complete, the viscous mixture was stirred for 30 min at 90°C. The di-α-sulfosebacinic acid di-methanol ester thus produced was identified using ¹³C NMR (90 MHz, in dimethylsulfoxide). In the second step, the di-α-sulfosebacinic acid di-methanol ester was heated to 85°C and slowly added (0.15 mol in 2 h) to 0.9 mol dodecanol at 120°C. After 6 h the produced methanol and the excess dodecanol were removed under vacuum. The reaction mixture was cooled and neutralized with 2 N sodium bicarbonate solution. Extraction with diethylether and removal of the solvent led to the raw Dim4 (purity ≈ 70%), with a yield of 70%. It was further purified by column chromatography on Kieselgel 60 with ethyl acetate/methanol (4 : 1 vol/vol) as

solvent. The elemental analysis of the purified Dim4 was satisfactory. The overall yield was 20%.

The samples of pyrene (fluorescent probe) and of dodecylpyridinium and hexadecylpyridinium chlorides (quenchers of the pyrene fluorescence) were the same as in previous studies (4). The water used throughout this work was purified using a Millipore apparatus Milli-RO 3Plus.

Concentrated stock solutions of the surfactants were used for preparing the samples of surfactant mixtures for time-resolved fluorescence quenching. Some turbidity developed in the 20 mM Dim4 stock solution, 12–24 h after its preparation. This solution was therefore filtered using a 100-nm hollow fiber filter and used right after filtration. The Dim4 concentration in the filtrate was determined by measuring its dry content. The filtration decreased the Dim4 concentration by 5–10%.

Methods

The cmc's were determined by spectrofluorometry from the variation of the pyrene intensity ratio I_1/I_3 with the surfactant concentration (4, 29). The fluorescence emission spectra were recorded using a Hitachi 4010 spectrofluorometer, operated at an excitation wavelength of 335 nm, with a bandpass of 1.5 nm both at the excitation and emission. The cmc's of the DTAB/12-2-12 mixture were determined by the electrical conductivity method. The conductances were measured using an automated balanced conductivity bridge Wayne–Kerr B905. These measurements were carried out at 25°C.

The micelle aggregation numbers were determined by means of the time-resolved fluorescence quenching technique using the previously described single-photon counting apparatus (30, 31). The measurements were performed at 25, 40, and 55°C with all mixtures except 12-2-12/C₁₂E₆, where the measurements were performed at 15, 20, and 25°C. The fluorescence decay curves were recorded in the absence and in the presence of quencher. The former yielded the pyrene fluorescence lifetime τ in the micellar environment. In most instances the fluorescence decay curves in the presence of quencher were found to have a long time slope which was identical to that in the absence of quencher, within the experimental error. This behavior indicated that the probe and quencher distributions were frozen on the fluorescence time scale (32–35). In this case the usual four-parameter decay equation was fitted to the decay curves. This fitting directly yielded the pyrene fluorescence lifetime τ in the micellar environment, the rate constant k_q for intramicellar quenching, and the ratio $R = [Q]/[M]$ where $[Q]$ and $[M]$ are the quencher and micelle molar concentrations (32–35). For the solutions of C₁₂E₆ at 20 and 25°C and of C₁₂E₈ at 55°C the long time part of the decay curve showed a slope larger in the presence than in the absence of quencher. This behavior indicated that probe and/or quencher migration between micelles occurred on the fluorescence time scale as was noted in a previous TRFQ investigation of these two surfactants (36). The equations appropriate to this situation (32–35) were used for the analysis of the decay curves, and again yielded the values of τ , R , and k_q . The total number N_T of

surfactant chains per micelle was obtained from the equation [4]

$$N_T = R(2C_D + C_{CS} - \text{cmc})/[Q], \quad [2]$$

where C_D and C_{CS} are the molar concentrations of the dimeric and of the conventional surfactants (ionic or nonionic). Note that the present measurements used values of $C_D + C_{CS}$ much larger than the cmc of the mixtures. Thus, the micelle composition was always close to the weighing-in composition of the surfactant mixture. The aggregation numbers of the dimeric surfactant and of the conventional surfactant in the mixed micelles, N_D and N_{CS} , respectively, were obtained from

$$\begin{aligned} N_D &= 2N_T X_D / (1 + X_D) \quad \text{and} \\ N_{CS} &= N_T (1 - X_D) / (1 + X_D), \end{aligned} \quad [3]$$

where $X_D = C_D / (C_D + C_{CS})$ is the dimeric surfactant mole fraction in the surfactant mixture. For mixtures of two conventional surfactants, the factor 2 in Eqs. [2] and [3] is removed.

Another problem occurred with Dim4, possibly connected with the problem of turbidity discussed above. The Dim4 solutions containing pyrene but no quencher showed nonlinear decay curves. This behavior cannot be satisfactorily explained at the present time. Similar nonlinear decays have been sometimes observed with surfactant-containing systems (37). Nevertheless, it was possible to fit the usual four-parameter decay equation to these curves and to obtain an apparent occupation number, R_p , and an apparent quenching rate constant in the absence of quencher, $k_{q,p}$. These values were used to correct the values of the occupancy number determined for the same solution in the presence of quencher, R_q . The aggregation numbers were obtained by inserting in Eq. [2] a corrected value of R_q taken as

$$R_{q,\text{corr}} = R_q - R_p [k_{q,p} / (k_{q,p} + k_{q,q})], \quad [4]$$

where $k_{q,q}$ is the quenching rate constant determined in the presence of quencher. Equation [4] has no rigorous basis. However, it correctly predicts that $R_{q,\text{corr}} \rightarrow R_q$ as $k_{q,p}/k_{q,q} \rightarrow 0$ or as $R_p \rightarrow 0$. Other methods of correcting the data in a situation similar to ours, i.e., when the decay found for the system containing only pyrene and no quencher is not linear, have been used (37).

The solutions for TRFQ studies were prepared as previously described (28, 30, 38). The fluorescence decay curves were recorded after complete removal of the air solubilized in the solution by three freeze–pump–thaw cycles. This was followed by a saturation of the solution with nitrogen, in order to avoid its boiling during measurements at 40 or 55°C. The fluorescence cell which permits the complete removal of the air saturating the solutions and their regassing has been described (38).

The mixed micelle aggregation numbers were measured in six mixtures, keeping the total molar surfactant concentration C_T constant while varying the molar fraction of the ionic component. This mole fraction is referred to as X_D for both the dimeric

and the conventional surfactants, below. The investigated mixtures and the values of C_T were as follows: DTAB/ $C_{12}E_8$ and SDS/ $C_{12}E_8$, $C_T = 100$ mM; 12-2-12/ $C_{12}E_8$, 12-3-12/ $C_{12}E_8$, and Dim4/ $C_{12}E_8$, $C_T = 20$ mM; and 12-2-12/ $C_{12}E_6$, $C_T = 10$ mM. For all these mixtures the value of C_T is well above the value of the cmc of the pure surfactants or of the surfactant mixtures.

RESULTS AND DISCUSSION

Cmc

Figures 1A and 1B show the variations of the electrical conductivity and of the I_1/I_3 ratio with the surfactant concentration, C_D , for Dim3 and Dim4, respectively. For Dim3 the conductivity plot in Fig. 1A yields a cmc value of 5.7 mM, which corresponds to the break in the plot. This concentration is seen to correspond to the end of the decrease in I_1/I_3 vs C_D plot, as it has been observed in previous studies of surfactants with high cmc values (29). The conductivity plot in Fig. 1B shows that the cmc of Dim4

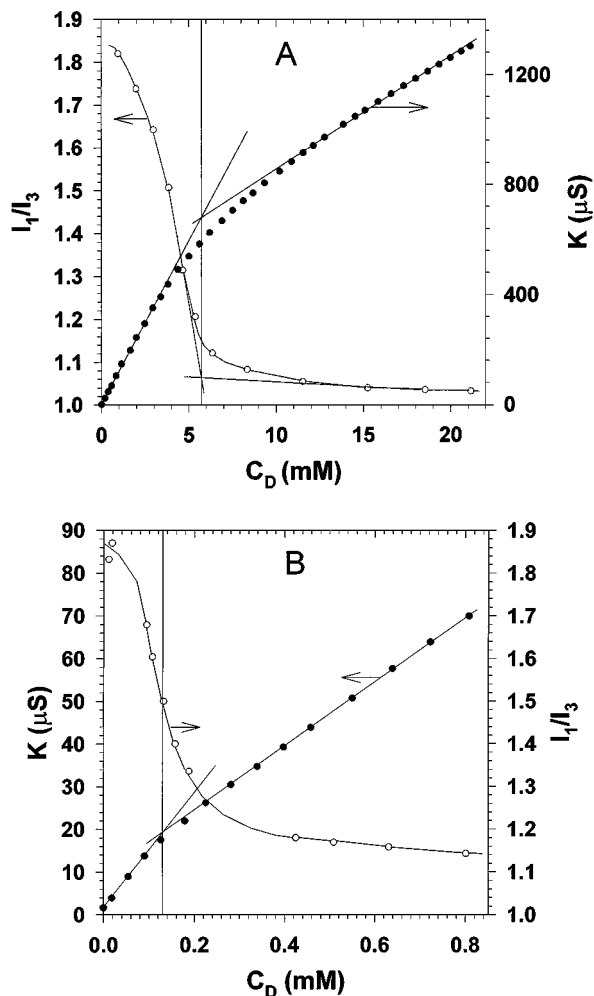


FIG. 1. Cmc determination by measurements of conductivity K (●) and fluorescence intensity ratio I_1/I_3 (○) for Dim3 (A) and Dim4 (B) at 25°C. In each figure the vertical line corresponds to the cmc.

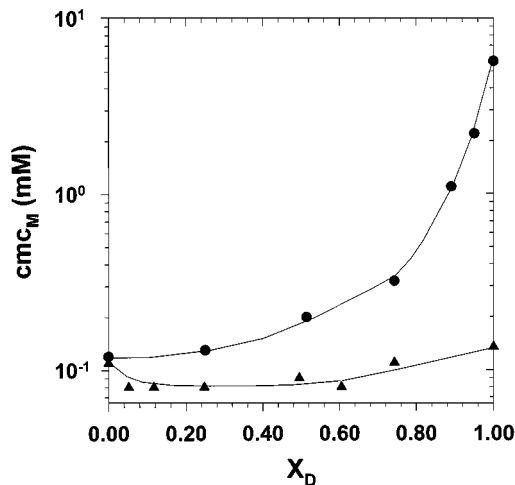


FIG. 2. Variation of the cmc_M of the Dim3/ $C_{12}E_8$ (●) and the Dim4/ $C_{12}E_8$ (▲) mixtures with the dimeric surfactant mole fraction at 25°C. The solid lines are guides to the eyes.

is relatively low, around 0.13 mM. This concentration closely corresponds to the midpoint of the decrease in the I_1/I_3 vs C_D plot. A similar result was already reported in previous studies which compared the cmc values obtained from the variations of conductivity and of I_1/I_3 for surfactants or surfactant mixtures of low cmc value (4, 39). The lower cmc value of Dim4 with respect to Dim3 mainly reflects the longer alkyl chain of Dim4. The difference in the nature of the spacer groups of the two surfactants (hydrophilic for Dim3 and hydrophobic for Dim4) may also contribute to this difference.

Most of the mixtures investigated in the present study contained the nonionic surfactants $C_{12}E_6$ or $C_{12}E_8$. The pyrene fluorescence probing method was therefore used since the conductivity method is not operative for determining the cmc of these surfactants and surfactant mixtures at low ionic surfactant content. The cmc value of these mixtures was taken as the concentration corresponding to the midpoint of the decrease in the I_1/I_3 vs concentration plot. This procedure resulted in an error on the cmc values of up to $\pm 10\%$, i.e., larger than if the cmc was obtained by conductivity. The conductivity method was used only for the 12-2-12/DTAB mixture as it involves two ionic surfactants.

Table 1 lists the cmc values of the six investigated mixtures at 25°C. Figure 2 shows the composition dependence of the cmc of the Dim3/ $C_{12}E_8$ and Dim4/ $C_{12}E_8$ mixtures as an illustration of the type of data obtained. The Dim4/ $C_{12}E_8$ mixture was the only one that showed synergism, i.e., where the cmc's of some mixed systems are lower than the cmc's of the pure surfactants.

The cmc's of the mixtures have been analyzed using Eqs. [5] and [6] derived for nonideal surfactant mixtures (40), in order to extract the parameter of interaction between surfactants, β ,

$$\frac{x_D^2}{(1-x_D)^2} \frac{\log(X_D cmc_D / x_D cmc_D)}{\log[(1-X_D) cmc_M / (1-x_D) cmc_D]} = 1 \quad [5]$$

TABLE 1
Cmc Values in the Investigated Mixtures at 25°C as a Function of Composition^a

Dim3/C ₁₂ E ₈ ^b β = -1.3								
X _D (M/M)	1.00	0.953	0.894	0.760	0.509	0.265	0.00	
cmc _M (mM)	5.7	2.19	1.11	0.228	0.205	0.131	0.115	
Dim4/C ₁₂ E ₈ ^b β = -1.7								
X _D (M/M)	1.00	0.75	0.605	0.495	0.248	0.117	0.052	0.00
cmc _M (mM)	0.13	0.11	0.08	0.09	0.08	0.08	0.08	0.11
DTAB/C ₁₂ E ₈ ^b β = -1.7								
X _D (M/M)	1.00	0.924	0.668	0.533	0.348	0.00		
cmc _M (mM)	14	2.15	0.484	0.275	0.196	0.125		
12-2-12/DTAB ^c β = -2.2								
X _D (M/M)	1.00	0.819	0.479	0.326	0.112	0.0536	0.00	
cmc _M (mM)	0.90	1.006	1.59	2.04	2.77	3.89	15.5	
12-2-12/C ₁₂ E ₈ ^b β = -0.9								
X _D (M/M)	1.00	0.92	0.75	0.50	0.25	0.00		
cmc _M (mM)	0.85	0.532	0.295	0.165	0.127	0.12		
12-3-12/C ₁₂ E ₈ ^b β = -0.8								
X _D (M/M)	1.00	0.92	0.75	0.50	0.25	0.00		
cmc _M (mM)	0.858	0.555	0.28	0.179	0.125	0.12		

^a X_D (M/M) = C_D/(C_D + C_{CS}), mole fraction in mole per mole. Mole fraction in eq/eq: X_{D,eq} = 2X_D/(1 + X_D). Cmc of the mixture in equivalent per liter: cmc_{M,eq} = cmc_M(1 + X_D).

^b From fluorescence.

^c From conductivity.

and

$$\beta = \left[\log \frac{X_D \text{cmc}_M}{x_D \text{cmc}_D} \right] / (1 - x_D)^2. \quad [6]$$

In these equations X_D and x_D are the mole fractions of the dimeric surfactant in the mixture and in the micelles, respectively, cmc_D is the cmc of the dimeric surfactant, and cmc_M is that of the mixture of composition X_D.

Table 1 gives the average values of β for the different mixtures. The error on these values is rather large and is estimated to be ±1.5, owing to the relative inaccuracy of the cmc determinations. Recently, several papers discussed the approximation involved in using a single value of β to account for the cmc of binary surfactant mixtures in the whole range of composition (22, 41–44). For mixtures of an ionic and a nonionic surfactant it has been argued that the interaction parameter must be a function of the composition because the electrostatic contribution to β varies much with composition (44). Large differences in surfactant head group size can also result in a composition-dependent interaction parameter (43). However, the quality of our data does not warrant analysis based on a composition-dependent value of β.

The values of β for the mixtures of Dim3 and Dim4 with C₁₂E₈ are rather close. They are somewhat less negative than the values measured for the mixtures of the anionic dimeric surfactant Dim1 with C₁₂E₅ and C₁₂E₈ (4). The β values for the three anionic dimeric surfactant/C₁₂E₈ mixtures are all less negative than for the reference mixture SDS/C₁₂E₈ for which β = -3.9 (45). Note, however, that the much less negative value of -2.7 has been reported for the mixture SDS/C₁₂E₆ (23). The val-

ues of β for the mixtures of DTAB, 12-2-12 and 12-3-12, with C₁₂E₈ are all quite close. The value for the 12-2-12/C₁₂E₆ mixture has been reported to be -2.2 (11), still in the error range. A last comment concerns the monomer/dimer mixture DTAB/12-2-12. Mixed micellization in this mixture has been evidenced by transmission electron microscopy at cryogenic temperature (46). Small-angle neutron scattering (47) has been used to characterize the formation of mixed micelles in this mixture. The value β = -2.2 found for this mixture is larger than the values reported for other binary mixtures of surfactants of like charge which often behave as nearly ideal mixtures (47, 48). This different behavior of the monomer/dimer mixture may be due to the dimeric nature of one component of the mixture.

Micelle Aggregation Numbers in Cationic Dimeric/Nonionic Surfactant Mixtures

The measurements of aggregation numbers involved mixtures of surfactants that all contained the dodecyl chain, 12-2-12/C₁₂E₆, 12-2-12/C₁₂E₈, 12-3-12/C₁₂E₈, and DTAB/C₁₂E₈. These mixtures were selected as they permit the investigation of the effect of the spacer length of the dimeric surfactant and of the head group of the nonionic surfactant on the mixed micelle aggregation number. They also permit one to compare the behavior of a monomeric conventional surfactant (DTAB) to that of a dimeric surfactant (12-2-12 or 12-3-12) when mixed to the same nonionic surfactant (C₁₂E₈). Indeed, DTAB can be formally considered as the monomer of 12-2-12 and 12-3-12. The effect of temperature was also investigated. The values of the cmc used in the calculation of the aggregation numbers by means of Eq. [2] are those listed in Table 1. The values reported by Esumi *et al.*

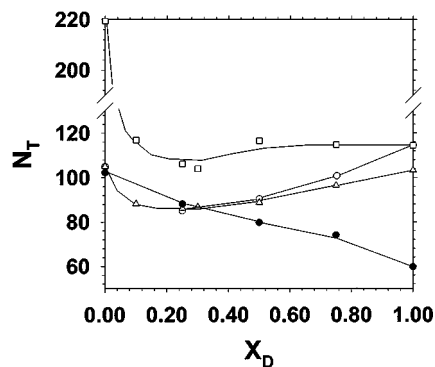


FIG. 3. Variation of the total aggregation number of the mixed micelles with the mole fraction of the ionic surfactant in the mixture: DTAB/ $C_{12}E_8$ (\bullet ; $C_T = 100$ mM); 12-2-12/ $C_{12}E_8$ (\circ ; $C_T = 20$ mM); 12-2-12/ $C_{12}E_6$ (\square ; $C_T = 10$ mM); and 12-3-12/ $C_{12}E_8$ (\triangle ; $C_T = 20$ mM). $T = 25^\circ\text{C}$. The solid lines are guides to the eyes.

(11) were used for the 12-2-12/ $C_{12}E_6$ mixtures. All these values refer to 25°C while some measurements of aggregation numbers were performed at other temperatures. However, the surfactant concentrations used were much larger than the cmc's. Thus the change of cmc with temperature resulted in a negligible error on the aggregation numbers.

Effect of the mixture composition on the mixed micelle aggregation number. In the representation of the results N_T , the number of surfactant chains per micelle, was preferred to $N_S = N_T/(1 + X_D)$, the number of surfactants per micelle. Indeed, the N_T values permit an easier comparison of the volumes of the micelles of different surfactants since the micelle volume is proportional to the number of surfactant chains.

Figure 3 shows the variation of the total aggregation number N_T with the mixture composition, X_D , for the four mixtures investigated at 25°C . In the reference mixture DTAB/ $C_{12}E_8$, N_T is seen to decrease gradually with increasing DTAB mole fraction. The decrease of N_T is obviously associated with the increased average repulsive interaction between surfactant head groups with increasing X_D , as nonionic surfactants are progressively replaced by ionic surfactants. As a consequence the average optimal surface area per hydrophilic group increases and the number of surfactant chains per micelle decreases. The smallest aggregation number corresponds to the highest surface charge density, i.e., pure DTAB micelles. The addition of dimeric surfactants to $C_{12}E_8$ also initially causes a decrease of N_T , for the same reason as additions of DTAB. In fact, the decrease of N_T is about the same up to $X_{D,\text{eq}} \approx 0.20$, upon additions of DTAB, 12-2-12 and 12-3-12, in a plot (not shown) of N_T against the fraction $X_{D,\text{eq}} = 2X_D/(1 + X_D)$ of ionic surfactant expressed in equivalent per total equivalent. Hence, the type of the cationic surfactant (monomeric or dimeric) does not influence the size of the mixed micelles in this region, up to $X_D \approx 0.12$. Then N_T goes through a minimum at $X_D \approx 0.15$ and increases with X_D up to the value of the aggregation number of the pure dimeric surfactant micelle. It is noteworthy that the plots for the 12-2-

12/ $C_{12}E_8$ and 12-3-12/ $C_{12}E_8$ mixtures are rather close in the range $0 < X_D < 0.5$. At higher mole fraction the effect of the ionic surfactant becomes predominant and a small difference occurs between the two plots because the micelle aggregation number is larger for 12-2-12 than for 12-3-12 (50). The difference would be even larger if the two surfactants were studied at the same concentration of 20 mM, while in fact the results for 12-2-12-containing mixtures refer to a concentration of 10 mM. Indeed, the aggregation number of 12-2-12 micelles is known to increase very rapidly with concentration (50). It remains that the small difference between the two plots is well explained by the difference of micelle size of the two dimeric surfactants. The effect of the spacer length (increase of the aggregation number upon decreasing spacer length (50)) is thus also found for the mixtures at high mole fraction of dimeric surfactant.

The comparison of the results for the 12-2-12/ $C_{12}E_6$ and 12-2-12/ $C_{12}E_8$ mixtures in Fig. 3 shows that the smaller hydrophilic head group of $C_{12}E_6$ with respect to $C_{12}E_8$ leads to the formation of larger micelles at any given value of X_D . This is particularly clear at low X_D , where the effect of the nonionic surfactant dominates the behavior of the system. The plot for the 12-2-12/ $C_{12}E_6$ mixture also has a minimum at a value of X_D slightly larger than that for the 12-3-12/ $C_{12}E_8$ mixtures (0.25 against 0.20). This plot apparently shows a maximum of small amplitude at $X_D \approx 0.50$, but keeping in mind the experimental error it is difficult to say how reliable this is. Nevertheless, the presence of 12-2-12 clearly influences much more strongly the size of $C_{12}E_6$ micelles than that of $C_{12}E_8$ micelles. This is so because at 25°C the $C_{12}E_6$ solution is much closer to its cloud temperature (50°C) than the $C_{12}E_8$ solution (77°C) (51). The micelle size is then much more sensitive to additives that increase the cloud temperature (36). Note that the aggregation behavior in the 12-2-12/ $C_{12}E_6$ mixture has been investigated by light scattering (11). The reported results differ much from those in Fig. 3. The N_T vs C_D plot shows a wide minimum in the range $0.2 < X_D < 0.8$, with N_T values around 20–40. Also, the N_T value reported for the pure $C_{12}E_6$ micelle is of only 120 as compared to 220 in the present work, and 280 at 25 mM in the presence of 0.1 N NaCl (the presence of NaCl is expected to result in a moderate micelle growth) (9). However, the N_T values reported in Ref. (11) refer to the cmc of the mixtures, and one expects the values of N_T at the cmc to be lower than at the concentration of 10 mM (this work) or 25 mM (9). Besides, the cmc's did not show clearly in the reported surface tension vs concentration plots in Ref. (11). Errors on the cmc values to which the light scattering data were extrapolated, and such extrapolations for systems where the aggregate size is dependent on concentration, as is the case here, may contribute to the observed differences.

The size of the mixed micelles in the studied solutions is mainly determined by the repulsions between head groups (of steric origin for oxyethylene head groups and of electrostatic origin for quaternary ammonium head groups) and also by the packing parameters of the surfactants making up the mixture. As discussed above the initial effect of introducing an ionic

surfactant into a nonionic surfactant micelle is to increase the average repulsion between head groups and, thus, decrease the micelle size, as is seen in Fig. 3. At low X_D the added cationic surfactants are probably entirely or nearly entirely dissociated, i.e., no counterions are bound by the micelles. Counterion binding by the mixed micelles starts only when X_D reaches a certain value (52–54).

Effect of temperature (T) on the mixed micelle aggregation number. It is known that an increase of T generally increases the aggregation number of nonionic micelles of the C_mE_n type (51) and decreases that of ionic micelles (55). When ionic and nonionic surfactants are mixed, the variation of the aggregation number of the mixed aggregates is mainly determined by the interplay of these two opposite tendencies as well as the interactions between the hydrophilic heads. Figures 4A–4C show the variation of the mixed micelle aggregation number with composition at different temperatures for the DTAB/ $C_{12}E_8$, 12-3-12/ $C_{12}E_8$ and 12-2-12/ $C_{12}E_6$ mixtures.

In the case of DTAB/ $C_{12}E_8$ mixtures, Fig. 4A, shows that N_T changes gradually with X_D and depends only little on T in the range $0.25 < X_D < 0.75$. The value of N_T for $C_{12}E_8$ micelles increases rapidly with temperature at $T > 40^\circ\text{C}$, in agreement with a previous report (36). This has been attributed to a decreased polarity of the ethoxylated chains (56).

Figure 4B shows the results for 12-3-12/ $C_{12}E_8$ mixtures. The minimum in the N_T vs X_D plot present at 25°C , disappears at 40 and 55°C . The N_T is seen to be nearly independent of T at $X_D \approx 0.08$. At lower mole fractions N_T increases with T as for nonionic surfactants. At higher mole fractions N_T decreases upon increasing T , indicating that the effect of the ionic dimeric surfactant is predominant in this range.

The experiments with 12-2-12/ $C_{12}E_6$ micelles were performed at lower temperatures because pure $C_{12}E_6$ micelles grow rapidly with T (36), and at above 25°C the aggregation numbers become too large to be measured by time-resolved fluorescence quenching. The results in Fig. 4C show that increasing the temperature from 15 to 25°C strongly increases the aggregation number of pure $C_{12}E_6$ micelles but does not significantly change the size of the mixed aggregates. All curves have the same shape, with a minimum at around $X_D = 0.25$, as in the case of the 12-3-12/ $C_{12}E_8$ mixture at 25°C . The aggregation number of 12-2-12 micelles could not be measured by TRFQ at 15 and 20°C .

Intramolecular quenching rate constants k_q . The values of k_q are obtained from the fit of the decay curves to the appropriate decay equations (see above). They can provide information on the micellar properties (57). Thus, k_q decreases upon increasing micellar size as $1/N_T^a$ (with $a \approx 1$ for spherical or spheroidal micelles and larger than 1 for elongated micelles) (58, 59). The k_q also decreases upon increasing viscosity of the probe/quencher micellar environment (microviscosity $\bar{\eta}$) (57). Figure 5 shows the variations of k_q with composition for the four cationic surfactant/nonionic surfactant mixtures investigated at 25°C . The results at the other temperatures (not shown) are quite

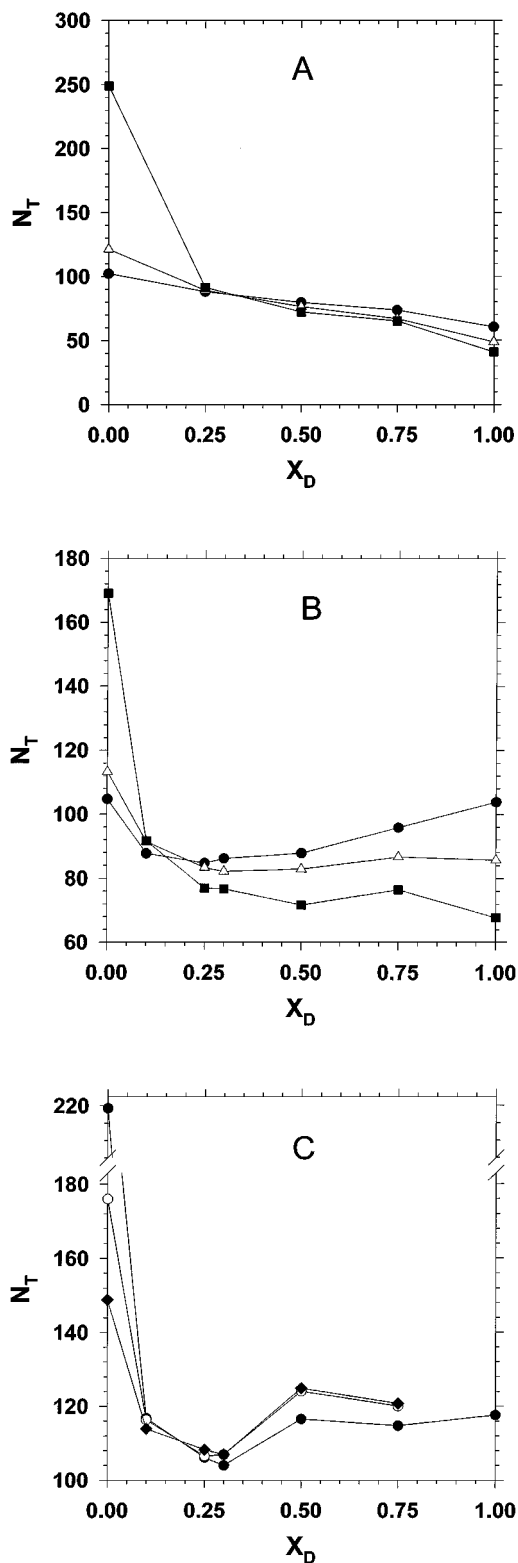


FIG. 4. Variation of the total aggregation number of the mixed micelles with the mole fraction of the ionic surfactant in mixtures of: (A) DTAB/ $C_{12}E_8$ ($C_T = 100$ mM) at 25°C (●), 40°C (△), and 55°C (■); (B) 12-3-12/ $C_{12}E_8$ ($C_T = 20$ mM) at 25°C (●), 40°C (△), and 55°C (■); and (C) 12-2-12/ $C_{12}E_6$ ($C_T = 10$ mM) at 15°C (◆), 20°C (○), and 25°C (●). The solid lines are guides to the eyes.

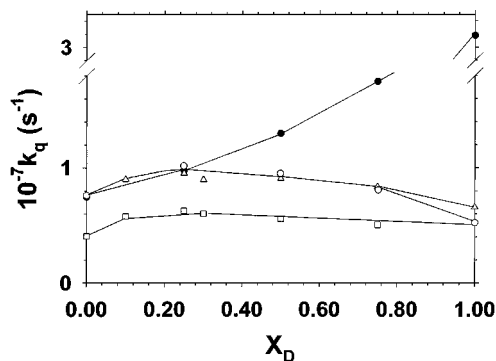


FIG. 5. Variation of the intramicellar quenching rate constant in the mixed micelles with the mole fraction of the ionic surfactant in the mixture: DTAB/ $C_{12}E_8$ (●; $C_T = 100$ mM); 12-2-12/ $C_{12}E_8$ (○; $C_T = 20$ mM); 12-2-12/ $C_{12}E_6$ (□; $C_T = 10$ mM); and 12-3-12/ $C_{12}E_8$ (△; $C_T = 20$ mM). $T = 25^\circ\text{C}$. The solid lines are guides to the eyes.

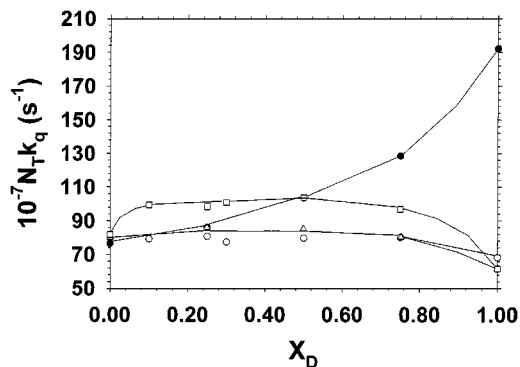


FIG. 6. Variation of the product $N_T k_q$ (proportional to the reciprocal microviscosity) for the mixed micelles with the mole fraction of the ionic surfactant in the mixture: DTAB/ $C_{12}E_8$ (●; $C_T = 100$ mM); 12-2-12/ $C_{12}E_8$ (○; $C_T = 20$ mM); 12-2-12/ $C_{12}E_6$ (□; $C_T = 10$ mM); and 12-3-12/ $C_{12}E_8$ (△; $C_T = 20$ mM). $T = 25^\circ\text{C}$. The solid lines are guides to the eyes.

similar. The value of k_q is the largest for the pure DTAB micelles, as is expected keeping in mind that their aggregation numbers are the smallest. Similarly the value of k_q is the smallest for the system with the largest micelles, that is, pure $C_{12}E_6$. The correlations between the variations of N_T in Fig. 3 and of k_q in Fig. 5 are obvious. Thus, for the DTAB/ $C_{12}E_8$ mixture, N_T decreases and k_q increases upon increasing X_D , taking intermediate values between those measured in the pure $C_{12}E_8$ and DTAB micelles. Both the N_T vs X_D and the k_q vs X_D plots for the 12-2-12/ $C_{12}E_8$ and 12-3-12/ $C_{12}E_8$ mixtures are nearly coincident, up to $X_D \approx 0.5$. The main difference in the k_q vs X_D plots occurs at $X_D = 1$ and reflects the larger size of the 12-2-12 micelles with respect to 12-3-12 micelles (50). Also the 12-2-12/ $C_{12}E_6$ mixture is characterized by the largest values of N_T and, as expected, by the smallest values of k_q , in the whole range of X_D . Last, in every instance where the N_T vs X_D plot goes through a minimum, the corresponding k_q vs X_D plot goes through a maximum.

Thus, the correlation between the values of N_T and of k_q is very good. However, k_q depends on N_T and also on the micelle microviscosity (27, 57). A separation of the effects of these two parameters can be achieved only in a semiquantitative manner at the present time. Indeed for spheroidal micelles k_q varies as $1/N_T$ and to a first approximation the product $N_T k_q$ is proportional to the reciprocal of the micelle microviscosity, i.e., $1/\bar{\eta}$ (56–58). For the mixtures investigated the measured aggregation numbers are all between 60 and 120, except for $C_{12}E_6$, at all temperatures investigated, and for $C_{12}E_8$ at 55°C . For surfactants with a dodecyl chain the aggregation number of the maximum spherical micelles is around 60. Thus the micelles in the mixtures are spherical or spheroidal, except for the pure nonionic surfactants at high temperature, and the variations of product $N_T k_q$ can yield information on the variations of the micelle microviscosity. Figure 6 illustrates these variations at 25°C . These results suggest that for the three mixtures containing a dimeric surfactant the microviscosity depends relatively little on the nature of the surfactant, whether monomeric or dimeric, in the whole

range of X_D values. Indeed the differences of microviscosity are never larger than about 10–15%. The microviscosity of the $C_{12}E_8$ /DTAB mixture is also close to that of the other three mixtures up to $X_D = 0.5$; then it becomes smaller at higher mole fraction. This difference reflects the larger micelle microviscosity of dimeric surfactants with respect to the corresponding monomeric surfactants (60).

In view of the results in Figs. 3, 5, and 6 it appears that for the investigated mixtures the micellar properties are determined mainly by the nonionic surfactant up to $X_D \approx 0.25$ and by the ionic component at higher mole fraction.

Micelle Aggregation Numbers in Anionic Dimeric/Nonionic Surfactant Mixtures

The measurements concerned the Dim4/ $C_{12}E_8$ and SDS/ $C_{12}E_8$ mixtures. SDS can be considered to correspond roughly to the monomer of Dim4. The reported values of the cmc of the SDS/ $C_{12}E_8$ mixture (45) were used for calculating the mixed micelle aggregation number.

Figure 7 displays the variation of the total aggregation number N_T with the mole fraction of the ionic surfactant for the two

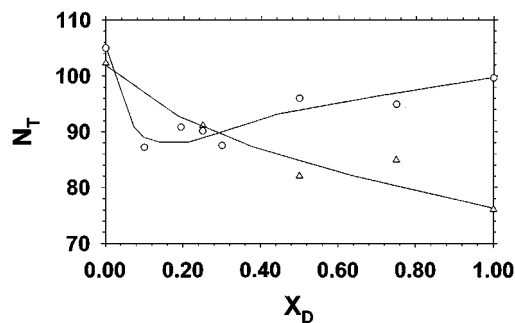


FIG. 7. Variation of the total aggregation number of the mixed micelles with the mole fraction of the ionic surfactant in the mixture: SDS/ $C_{12}E_8$ (△; $C_T = 100$ mM); Dim4/ $C_{12}E_8$ (○; $C_T = 20$ mM). $T = 25^\circ\text{C}$. The solid lines are guides to the eyes.

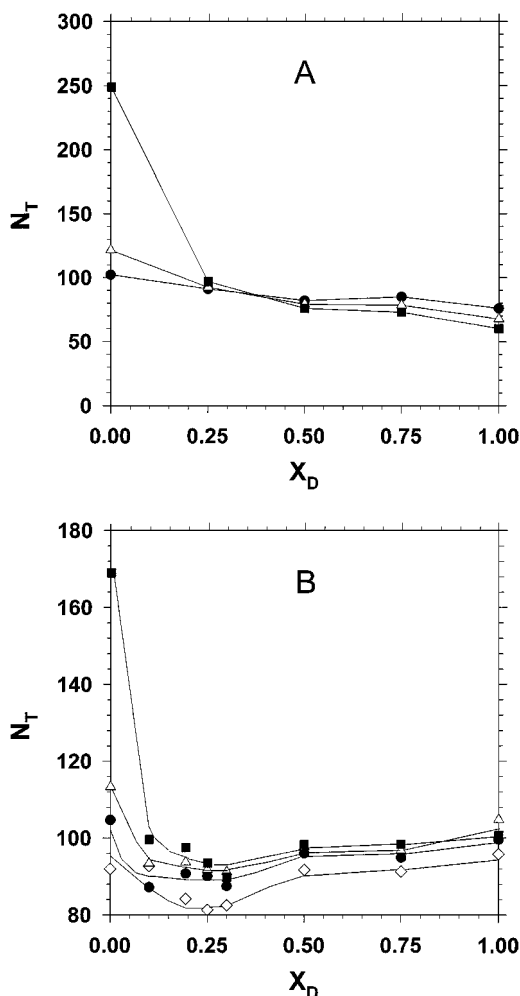


FIG. 8. Variation of the total aggregation number of the mixed micelles with the mole fraction of the ionic surfactant in the mixture: (A) SDS/C₁₂E₈ ($C_T = 100$ mM) at 25 (●), 40 (△), and 55°C (■); (B) Dim4/C₁₂E₈ ($C_T = 20$ mM) at 10 (◇), 25 (●), 40 (△), and 55°C (■). The solid lines are guides to the eyes.

mixtures. The effect of temperature on the N_T vs composition plots is represented in Figs. 8A and 8B. The value of N_T for the SDS/C₁₂E₈ mixture decreases continuously from the value for the nonionic surfactant to that of SDS, at all three temperatures investigated. The plots in Fig. 8A are very similar to those for the DTAB/C₁₂E₈ (Fig. 4A). In fact, at a given T , the values of N_T are about the same for the DTAB/C₁₂E₈ and SDS/C₁₂E₈ mixtures up to $X_D \approx 0.5$ (compare Figs. 4A and 8A). Thus, in this range the observed variations of N_T are essentially due to the modification of the interactions between the nonionic head groups of C₁₂E₈ and of the packing of this surfactant upon incorporation of the ionic surfactant in the micelles. At higher mole fractions a small difference occurs, which reflects the slightly larger micelle aggregation number of SDS with respect to DTAB. The plot for the Dim4/C₁₂E₈ mixture shows a minimum, similarly to most of the plots for the cationic dimeric surfactant/C₁₂E₈ mixtures. The presence of a minimum in the N_T vs composition plot has

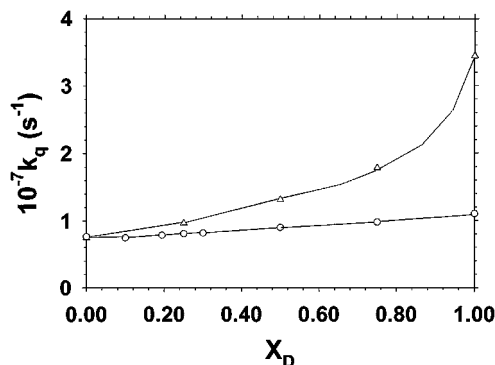


FIG. 9. Variation of the intramicellar quenching rate constant in the mixed micelles with the mole fraction of the ionic surfactant in the mixture: SDS/C₁₂E₈ (△; $C_T = 100$ mM); Dim4/C₁₂E₈ (○; $C_T = 20$ mM). $T = 25^\circ\text{C}$. The solid lines are guides to the eyes.

been reported for other binary surfactant mixtures in addition to the systems investigated in the present study (4, 11). The occurrence of a maximum has also been reported in two instances (9, 21). The first one concerns the C₁₂E₆/SDS mixture in the presence of 0.1 M NaCl (9). The maximum occurred at $X_D \approx 0.1$ and it was attributed to the subtle balance between steric and electrostatic interactions. A maximum was also reported for the mixtures of sodium dodecylsulfonate with zwitterionic surfactants of various alkyl chain length, in pure water and in the presence of 0.1 to 0.5 M NaCl (21). The reported results show that N_T is a maximum at $X_D \approx 0.7$, irrespective of the salt content. The explanation given for this maximum is close to that for the SDS/C₁₂E₆ mixture (9). The authors also observed that N_T was at maximum at a composition that closely corresponds to a minimum in the cmc vs composition plot (synergism in micelle formation). However, as seen above for the Dim4/C₁₂E₈ (see Fig. 8B) and in our previous studies (4), synergism in micelle formation may also result in a minimum in the N_T vs X_D plot. Thus, no general statement can be made at this stage concerning the relationship between synergism in micelle formation and the shape of the N_T vs X_D plot.

Figures 9 and 10 show the variations of k_q and of $N_T k_q$ with composition for SDS/C₁₂E₈ and Dim4/C₁₂E₈ mixtures. Here

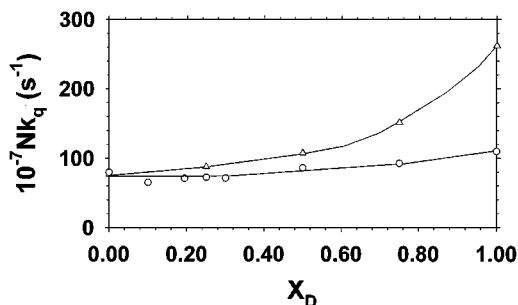


FIG. 10. Variation of the product $N_T k_q$ (proportional to the reciprocal microviscosity) for the mixed micelles in the mixtures SDS/C₁₂E₈ (△; $C_T = 100$ mM) and Dim4/C₁₂E₈ (○; $C_T = 20$ mM), with the mole fraction of the ionic surfactant at 25°C. The solid lines are guides to the eyes.

again the results are qualitatively similar to those for the cationic surfactant (conventional or dimeric)/C₁₂E₈ mixtures. In particular, the results in Fig. 10 suggest that the microviscosity in Dim4-containing micelles is greater than in SDS-containing micelles.

SUMMARY AND CONCLUSIONS

We have studied a number of binary mixtures of dimeric surfactants (12-2-12, 12-3-12, Dim3, and Dim4) and nonionic surfactants (C₁₂E₈ and C₁₂E₆) by measuring the cmc of the mixtures and the aggregation number of the mixed micelles as a function of the mixture composition and the temperature. Two reference mixtures, SDS/C₁₂E₈ and DTAB/C₁₂E₈, have also been investigated for the sake of comparison. Synergism in micelle formation (presence of a minimum in the cmc vs composition plot) has been observed for the Dim4/C₁₂E₈ mixture but not for the three cationic surfactant/C₁₂E₈ and Dim3/C₁₂E₈ mixtures. The aggregation numbers in the mixed reference systems SDS/C₁₂E₈ and DTAB/C₁₂E₈ vary monotonously from the value of pure C₁₂E₈ micelles to that of the pure ionic surfactant micelles. In contrast, the micelle aggregation number in the dimeric surfactant/C₁₂E₈ mixtures goes through a minimum at a low value of the dimeric surfactant mole fraction. The initial decrease of the aggregation number of the nonionic surfactant upon addition of ionic surfactant, up to a fraction of ionic surfactant of about 0.2 (in equivalent per total equivalent), depends little on the nature the surfactant, whether conventional or dimeric. This indicates that the decrease is due to the increased electrostatic repulsive interactions between head groups upon introduction of the ionic surfactant in the nonionic micelles. The combination of the values of the total aggregation number of the mixed micelles and of the intramicellar quenching rate constants shows that the microviscosity of the systems containing dimeric surfactants is greater than that of the reference systems.

ACKNOWLEDGMENTS

M.L. Sierra gratefully acknowledges the M.E.C. of the Spanish Government for financial support during her stay in Strasbourg. R. Alargova and I. Kochijashky thank Professors I. Ivanov and P. Kralchevsky from the LTPH (University of Sofia, Bulgaria) for allowing them to perform this work in Strasbourg. The financial support received under the European Program Tempus JEP 09789-95 is gratefully acknowledged.

REFERENCES

- Zana, R., in "Specialist Surfactants" (I. Robb, Ed.), Chap. 4, p. 81. Chapman Hall, London, 1997, and references therein.
- Zana, R., in "Structure-Performance Relationships in Surfactants" (K. Esumi and M. Ueno, Eds.), Chap. 6, p. 255. Dekker, New York, 1997, and references therein.
- Zana, R., in "Novel Surfactants. Preparation, Applications, and Biodegradability" (K. Holmberg, Ed.), Chap. 8, p. 241. Dekker, New York, 1998, and references therein.
- Zana, R., Lévy, H., and Kwetkat, K., *J. Colloid Interface Sci.* **197**, 370 (1998).
- Rosen, M. J., Zhu, Z. H., and Gao, T., *J. Colloid Interface Sci.* **157**, 254 (1993).
- Rosen, M. J., Gao, T., Nakatsuji, Y., and Masuyama, A., *Colloids Surf. A* **88**, 1 (1994).
- Liu, L., and Rosen, M. J., *J. Colloid Interface Sci.* **179**, 454 (1996).
- Nagai, K., and Esumi, K., *Colloids Surf. A* **94**, 97 (1995).
- Shiloah, A., and Blankschtein, D., *Langmuir* **14**, 7166 (1998).
- Ciccarelli, D., Costantino, L., D'Errico, G., Paduano, L., and Vitagliano, V., *Langmuir* **14**, 7130 (1998).
- Esumi, K., Miyazaki, M., Arai, T., and Koide, Y., *Colloids Surf. A* **135**, 117 (1998).
- Malliaris, A., Binana-Limbélé, W., and Zana, R., *J. Colloid Interface Sci.* **110**, 114 (1986).
- Ueno, M., Kimoto, Y., Ikeda, Y., Momose, H., and Zana, R., *J. Colloid Interface Sci.* **117**, 179 (1987).
- Muto, Y., Esumi, K., Meguro, K., and Zana, R., *J. Colloid Interface Sci.* **120**, 162 (1987).
- Zana, R., Muto, Y., Esumi, K., and Meguro, K., *J. Colloid Interface Sci.* **123**, 502 (1988).
- Velazquez, M., and Costa, S., *J. Chem. Soc. Faraday Trans.* **86**, 4043 (1990).
- Vethamuthu, M. S., Almgren, M., Mukhtar, E., and Bahadur, P., *Langmuir* **8**, 2396 (1992).
- Li, G.-Z., Li, F., Zheng, L.-Q., and Wang, H.-L., *Colloids Surf. A* **76**, 257 (1993).
- Suzuki, K., Hasegawa, T., Takamura, Y., Takahashi, K., Asano, H., and Ueno, M., *Langmuir* **12**, 5536 (1996).
- Almgren, M., Wang, K., and Asakawa, T., *Langmuir* **13**, 4535 (1997).
- Li, F., Li, G.-Z., and Chen, J.-B., *Colloids Surf. A* **145**, 167 (1998).
- Rodenas, E., Valiente, M., and Villafraña, M. S., *J. Phys. Chem. B* **103**, 4549 (1999).
- Penfold, J., Staples, E., Thompson, L., Tucker, I., Hines, J., Thomas, R. K., Lu, J. R., and Warren, N., *J. Phys. Chem. B* **103**, 5204 (1999).
- Zana, R., Lévy, H., Danino, D., Talmon, Y., and Kwetkat, K., *Langmuir* **13**, 402 (1997).
- Zana, R., in "Mixed Surfactant System" (K. Ogino and M. Abe, Eds.), Chap. 12, p. 337. Dekker, New York, 1993.
- Zana, R., *J. Colloid Interface Sci.* **78**, 330 (1980).
- Lianos, P., Lang, J., and Zana, R., *J. Phys. Chem.* **86**, 1019 (1982).
- Zana, R., Benraou, M., and Rueff, R., *Langmuir* **7**, 1072 (1991).
- Frindi, M., Michels, B., and Zana, R., *J. Phys. Chem.* **96**, 8137 (1992); *Langmuir* **10**, 1140 (1994).
- Malliaris, A., Lang, J., and Zana, R., *J. Chem. Soc. Faraday Trans. 1* **82**, 109 (1986).
- Zana, R., Lévy, H., Papoutsis, D., and Beinert, G., *Langmuir* **11**, 3694 (1995).
- Infelta, P., *Chem. Phys. Lett.* **61**, 88 (1979).
- Tachiya, M., *Chem. Phys. Lett.* **33**, 289 (1975).
- Almgren, M., *Adv. Colloid Interface Sci.* **41**, 9 (1992).
- Gehlen, M., and De Schryver, F. C., *Chem. Rev.* **93**, 199 (1993).
- Zana, R., and Weill, C., *J. Phys. Lett.* **46**, L953 (1985).
- Vorobyova, O., Yekta, A., Winnik, M. A., and Lau, W., *Macromolecules* **31**, 8998 (1998).
- Binana-Limbélé, W., Doctorate thesis, Louis Pasteur University, Strasbourg, France, June 1989.
- Zana, R., and Lévy, H., *Colloids Surf. A* **127**, 229 (1997).
- Rubingh, D. N., in "Solution Chemistry of Surfactants" (K. L. Mittal, Ed.), Vol. 1, p. 337. Plenum, New York, 1979.
- Hoffmann, H., and Pössnecker, G., *Langmuir* **10**, 381 (1994).
- Maeda, H., *J. Colloid Interface Sci.* **172**, 98 (1995).
- Eads, C., and Robosky, L., *Langmuir* **15**, 2661 (1999).
- Reif, I., and Somasundaran, P., *Langmuir* **15**, 3411 (1999).
- Lange, H., and Beck, K. H., *Kolloid-Z. Z. Polym.* **251**, 424 (1973).
- Zana, R., and Talmon, Y., *Nature* **362**, 228 (1993).
- Schosseler, F., Anthony, O., Beinert, G., and Zana, R., *Langmuir* **11**, 3347 (1995).

48. Ikeda, N., Shanefuji, N., Lu, K. K., Aratono, M., and Motomura, K., *J. Colloid Interface Sci.* **164**, 439 (1994), and references therein.
49. Treiner, C., and Makayssi, A., *Langmuir* **8**, 794 (1992).
50. Danino, D., Talmon, Y., and Zana, R., *Langmuir* **11**, 1448 (1995).
51. Degiorgio, V., in "Physics of Amphiphiles: Micelles, Vesicles and Microemulsions" (V. Degiorgio and M. Corti, Eds.), p. 303. North Holland, Amsterdam, 1985.
52. Abuin, E., Lissi, E., Nunez, R., and Olea, A., *Langmuir* **5**, 753 (1989).
53. Treiner, C., Khodja, A., and Fromon, M., *J. Colloid Interface Sci.* **128**, 416 (1989).
54. Treiner, C., and Mannebach, M., *Colloid Polym. Sci.* **268**, 88 (1990).
55. Malliaris, A., Le Moigne, J., Sturm, J., and Zana, R., *J. Phys. Chem.* **89**, 2709 (1985).
56. Karlstrom, G., *J. Phys. Chem.* **87**, 4762 (1985).
57. Lianos, P., Lang, J., Strazielle, C., and Zana, R., *J. Phys. Chem.* **86**, 1019 (1982).
58. Van der Auweraer, M., and De Schryver, F. C., *Chem. Phys.* **111**, 105 (1987).
59. Van der Auweraer, M., Reekmans, S., Boens, N., and De Schryver, F. C., *Chem. Phys.* **132**, 91 (1989).
60. Zana, R., *J. Phys. Chem. B* **103**, 9117 (1999).