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A fluorescence probe study of gemini surfactants in aqueous solution: a comparison between *n-2-n* and *n-6-n* series of the alkanediyl-a,w-bis (dimethylalkylammonium bromides).

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Abstract: Two series of alkanediyl-a,w-bis (dimethylalkylammonium bromide (n-2-n and n-6-n; n=8, 10,12, and 16) have been synthesized and their micelles properties studied in aqueous solution using pyrene, pyrenecarboxaldehyde (PCA) and 1,8 anilinonaphtalene sulfonic acid sodium salt (ANS) as fluorescent probes. The micelles from these surfactants have been characterized on the basis of the information provided by micelle-solubilized fluorescent probes. The obtained results indicated that the surfactant concentration at which a marked decrease in I_{max} parameter of pyrenecarboxaldehyde (PCA) occurs corresponds to the CMC determined by conductimetric measurements. Changes in the emission spectra of ANS and PCA observed in the submicellar range for both surfactants series (n-2-n and n-6-n) were interpreted as formation of pre-aggregates. It was found that the dimeric surfactants with long spacer (s= 6) form more hydrated aggregates when compared with those formed by the n-2-n and C_nTAB surfactants series. This was attributed to a more difficult packing of n-6-n surfactant molecules to form micelles.

Keywords: Gemini surfactants; Dimeric Surfactants; Pyrene; Premicellar aggregation;

Introduction

The expression gemini surfactant was first used by Menger and Litau to denote bis-surfactants made up of two amphiphilic moieties connected to the head groups by the rigid spacers benzene and stilbene [1]. However these kind of surfactants were first studied by Bunton et al. investigating their catalytic effects on nucleophilic substitutions[2]. Recently gemini surfactants have been subject of a extensive investigation because of their unique properties such as higher surface activity, improvements in the antibacterial activity and others potential applications which have been recently reviewed by Svenson [3], Zana [4] and Menger [5]. The alkanediyl-a,w-bis (dimethylalkylammonium bromides) are dimeric surfactants referred to in general as n-s-n surfactants, where n and s are the carbon numbers of the surfactant alkyl chain and of the polymethylene spacer group respectively. They present remarkable properties diminishing more efficiently both the superficial tension and the critical micellization concentration (CMC) [4-12]. Recent studies have also indicated that in aqueous solutions at concentrations below the CMC, ion pairing and pre-micelles may be formed [13,14]. Although premicellar aggregates have been evidenced for a long time with common cationic surfactants [15] the first evidence of premicellization in gemini surfactant solutions was provided by Menger et al. using anionic and cationic gemini surfactants [16]. The association in the submicellar range was reported for dimeric surfactants with rigid and flexible spacers [17] but this proposition has been refused for 12-s-12 surfactants with sd" 10 [14]. Also, the effects of the spacer groups on the aggregate properties are not completely understood. An increase in the spacer length does not lead to a monotonic decrease in CMC [18]. For alkanediyl-*a,w*-bis (dimethylalkylammonium bromide) surfactants

shorter spacer groups may align the hydrocarbon chains leading to formation of "conventional" micelles, similar to those formed by monomeric alkyltrimethylammonium bromides (C_nTABs). For longer spacers the hydrophobic character of the surfactant is increased but the expected trend observed for the common C_nTABs, i.e., a decrease in CMC, is not observed.

The purpose of the present work was to investigate the association of two series of alkanediyl-a,w-bis (dimethylalkylammonium bromide) surfactants (n-s-n; n=8-16 and s=2 and 6) using 1,8 anilinonaphtalene sulfonic acid sodium salt (ANS), pyrenecarboxaldehyde (PCA) and pyrene as fluorescent probes. These molecules were chosen because they have absorption, emission and lifetimes that depend on the microenvironment around them[19]. These properties can be correlated with the characteristics of the microenvironments and used to predict the existence and peculiarities of the micellar aggregates. Despite an extensive research on this kind of surfactants their properties remain under study due to complexity of their amphiphilic structures and studies concerning the premicellar association and their aggregates properties are important to elucidate their association in aqueous solution. This has motivated us to compare the aggregation behavior and micelles properties of the n-2-n and n-6-n series with those of the conventional *n*-alkyltrimethylammonium bromides, focusing how their aggregation in aqueous solution is affected by both the spacer group and alkyl lengths of the surfactants.

Experimental details

Chemicals

N,N,N',N'–Tetramethylethylenediamine(99,5%) and N, N, N', N' - Tetramethyl - 1,6–Hexanediamine(99%) were purchased from Aldrich. Bromoalkanes were purchased from Merck and used without further purification. Pyrene (Aldrich) and pyrene-3-carboxaldehyde (PCA, Aldrich) were purified by two recrystallizations from ethanol. The solvents employed were fluorescence spectroscopy grade (Merck,) and were used without further purification.

Synthesis and Characterization of the Surfactants.

The n-s-n series of bis quaternary ammonium surfactants(8-6-8, 10-6-10, 12-6-12, 16-6-16, 8-2-8, 10-2-10,12-2-12 and 16-2-16) were synthesized by reacting the appropiated bromoalkane with alkanediyl-a,w-bis(dimethylamine) following a slightly modified method employed by Zana et al [18]. The reactions were performed in dry methanol under reflux for 48h in the presence of 20% excess of bromoalkane. The products were recrystallized twice in different mixtures of ethanol-ethyl acetate depending of the length of the hydrocarbon chain and spacer group. The recrystallization was repeated three times to achieve a good purity for 8-s-8 and 10-s-10 surfactants. The obtained surfactants were checked by elemental analysis and NMR measurements. The NMR spectra were recorded on a Brucker AC200 MHz spectrometer at 25 ^{o}C. The surfactants were examined in 5% (w/v) solutions of deuterated water (D_2O) and the chemical shifts were referenced to trimethylsilane.

Absorption and Fluorescence Spectroscopies Measurements.

The absorption spectra of the probes in the presence of surfactants were measured on a Cary 100 spectrophotometer equipped with a Peltier system 1×1 at 25^{0}C. Surfactants from concentrated stock solutions were added to both the reference and the aqueous probe solutions ($5x10^{-6}$ M) under magnetic stirring and the absorption spectra were recorded after each addition. All fluorescence measurements were performed at 25.0 ± 0.1 ^{o}C on a Hitachi 4500 fluorescence spectrometer. CMC values were obtained by fluorescence measurements using pyrenecarboxaldehyde (PCA) $5x10^{-6}$ mol/dm^3 (except for th n=16 surfactants where PCA concentration was $5x10^{-7}$ mol/dm^3) from a stock solution ($1x10^{-2}$ mol/dm^3 in methanol). PCA was excited at 356 nm and the emission recorded from 370 to 650 nm. Fluorescence spectra were recorded after each addition and all the solutions were prepared in deionized water (Milli-Q). The ratio between the fluorescence intensities of peaks I (372.4 nm) and III (384 nm) of the emission spectrum of pyrene ($1x10^{-6}$ mol/dm^3), (I_1/I_3), was used to evaluate the polarity of the local environment [19]. The probe 1,8 anilinonaphtalene sulfonic acid sodium salt (1,8-ANS) 5.0 x 10^{-6} mol/dm^3, was used to monitor the aggregation process

and excited at 377 nm. Fluorescence spectra were recorded after each addition from 400 to 650 nm.

Conductimetric measurements

Conductivities were measured using an automated Digimed (DM31) conductimeter at 25^{0}C (±0.5). The surfactant concentration in the cell was increased by addition of 10-100 ml aliquots of a concentrated surfactant solution to 10 ml of the water solution. Values were recorded after each addition. CMC from conductimetric experiments were determined from the change in the slope of the plot of specific conductivity *vs*. surfactant concentration. The ionization degree a is fraction of charges of micellized surfactant ions not neutralized by bound counterions whose values were obtained from the variation of electrical conductivity, *K*, with surfactant concentration *C*, taking $(dK/dC)_{C>CMC}$ / $(dK/dC)_{C<CMC}$.

Results and Discussion

Synthesis and Characterization.

The elemental analyses and the NMR spectral data confirm the formation of the dimeric surfactants. Figure 1a shows the ^{1}H-NMR for surfactant 10-6-10, with a peak at 3.45 ppm corresponding to N^+-CH_2 protons from both the hydrocarbon chain and the spacer group. The peak at 3.23 corresponds to N^+-CH_3 protons and the peak centered at 1.85 ppm corresponds to 8 methylene protons in the b position (b-CH_2) with respect to N^+-$(CH_3)_4$. Peaks centered in 1.56 –1.4 ppm correspond to methylene protons from the hydrocarbon chain and protons from the spacer group, which were denoted in Figure 1b as q- CH_2 , g-CH_2 and $(CH_2)_n$. The terminal –CH_3 protons (w-CH_3) from the hydrocarbon chain appear as a triplet at *d* 0.95-1.01 ppm.

ANS absorption spectra and fluorescence steady-state experiments.

The addition of the dimeric surfactants to aqueous solution of ANS leads to significant changes in the absorption spectrum of this probe. It can be seen from fig 2 that in the presence of 12-6-12 surfactant all the ANS UV–vis. absorption spectra are red shifted. The increase of 12-6-12 concentration leads to a decrease in the original ANS absorption band concomitantly with the appearance of a new band around 378 nm. For this probe the modifications observed in the electronic spectrum can be ascribed to association of the probe with premicellar aggregates. The same kind of red shift has been recently observed for pyrene in the presence of 12-s-12 surfactants [20]. The dimeric surfactants also lead to abrupt changes in the emission spectrum of ANS. Figure 3 shows the fluorescence intensity and l_{max} of 1,8 ANS in the presence of increasing concentration of the 8-6-8 and 8-2-8 surfactants. In water the l_{max} for ANS was observed at 518 nm and in the presence of a small amount of surfactant a large blue shift to 484 nm was observed in the fluorescence spectrum. The new maximum emission at 484 nm corresponds to the probe solubilized in a hydrophobic microenvironment. This tendency was followed for

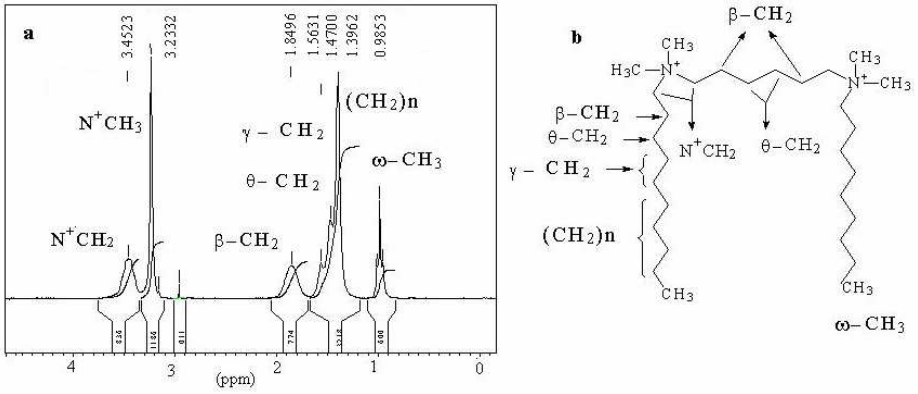

Figure 1 - a) ^{1}H-NMR spectrum of 10-6-10 surfactant in D_2O; b) structure and attribution of peaks to spectrum.

all n-6-n and n-2-n surfactants. Besides the blue shift a strong increase in the fluorescence quantum yield was observed, which indicates that the probe experiences a more constrained environment due to solubilization in a relatively nonpolar microenvironment. Due to the low range of surfactant concentration where these changes were observed, it may be suggested that electrostatic and hydrophobic interactions between ANS and surfactant molecules may lead to formation of ion pairs containing the ANS probe and a few surfactant molecules [21,22].

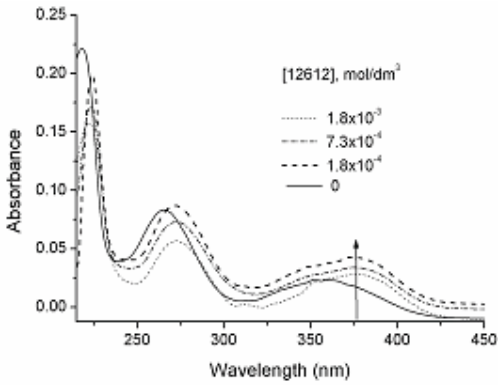

Figure 2- Absorption spectra of ANS in the presence of increasing concentration of 12-6-12.

After the blue shift to 484 nm the fluorescence of ANS increases continuously with the surfactant concentration, indicating that more probe molecules are solubilized in pre-micelles and/ or more hydrophobic cavities are formed to host the probes. As can be seen from figure 3 near the CMC the fluorescence quantum yield was moderately decreased due to the quenching provided by the bromide counterion condensation at the micelle surface.

PCA fluorescence steady-state experiments

The results obtained with pyrenecarboxaldehyde (PCA) in the presence of n-6-n surfactants were similar to those observed with ANS, however for concentrations above CMC the absorption spectra of PCA recover the spectral pattern observed in organic solvents such as methanol (data not shown). The presence of small amounts of n-6-n surfactants below the CMC shifts the maximum fluorescence from 475 to 470 nm and the fluorescence quantum yield increased continuously until the CMC is reached. On the other hand no significant shifts were observed for PCA in the submicellar range of n-2-n surfactants. In the submicellar range the maximum fluorescence of PCA in the presence of n-2-n surfactants remained almost constant and the fluorescence intensity decreased continuously (data not shown). These results also evidence the presence of premicellar aggregates containing a few molecules of surfactants and the fluorescent probe PCA. The fluorescence increase observed for PCA in the presence of the n-6-n surfactants may be attributed to better accommodation of this probe inside the premicellar aggregates, which in turn decreases the probe microenvironment polarity and also avoids the self-quenching commonly observed with pyrene and others hydrophobic probes [9]. In these premicellar aggregates the fluorescence emission of the probe is not efficiently quenched due to low concentration of bromide counterions in the surroundings of the premicelles.

The shift from 470 nm to about 455 nm was observed only above CMC, except for the surfactants 16-s-16, which presented a smaller shift to 466 nm (Fig. 4). This shift was also accompanied by an abrupt decrease in the fluorescence intensity (data not shown) resulting from the bromide counterions condensation at the micelle surface as that observed for the ANS probe. The presence of preaggregates in submicellar concentrations of dimeric surfactants has been suggested by Mathias et al. in a recent work using time resolved fluorescence spectroscopy[23], and thereafter their method was contested by Zana [24,25].

However our results indicate that for these surfactants premicellar aggregates can be postulated even though at a low surfactant concentration some aggregates could be induced by the probe. The CMC values were determined from the intercept of the tangents to the curve before and after the point of inflection in the plots of l_{max} of PCA vs. surfactant concentration (Fig. 4) and although slightly smaller than those obtained by conductimetric measurements (see Table 1), they are in good agreement with those determined for 16-2-16 and 12-2-12 using pyrene [26].

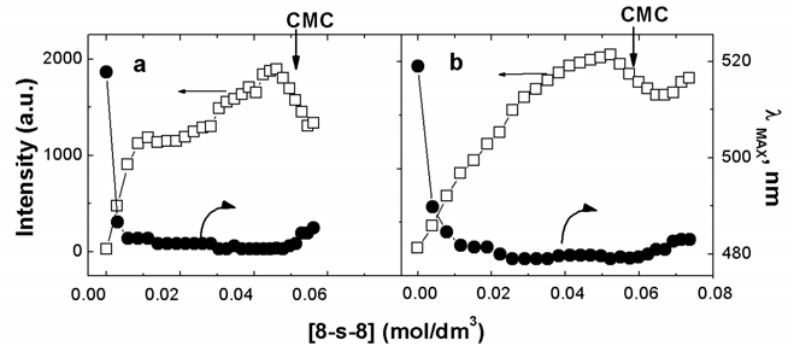

Figure 3. Fluorescence maximum (˜) and relative intensity (£) of ANS as a function of (a) 8-2-8 and (b) 8-6-8 concentration. The arrows at the top indicate the CMC determined by conductimetric measurements.

Pyrene fluorescence steady-state experiments

The Figure 5 shows the I_1/I_3 ratio of the pyrene fluorescence spectrum in the presence of increasing surfactant concentration (C). The I_1/I_3 ratio decreases slightly with both the surfactant concentration and the alkyl length of the surfactant (*n*). It is well known that pyrene exhibits a certain affinity for quaternary ammonium head groups, therefore the decrease for the I_1/I_3 ratios indicates that aggregation numbers increase and some water molecules are removed from the solvation shell of pyrene [32-34].

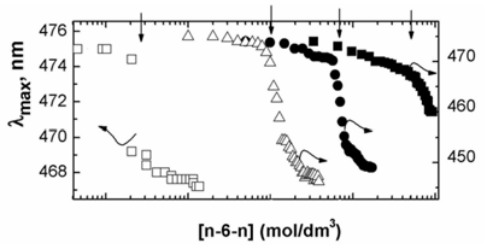

Figure 4. Fluorescence maximum of PCA as a function of n-6-n concentration: (¢)-8-6-8; (˜)10-6-10; (D)-12-6-12; (£)16-6-16. The arrows indicate the CMC values.

This behavior may be due to the increasing aggregation numbers (*N*) with concentration and this has been observed for dimeric surfactants having short as well as longer spacer groups [32, 33]. The most noticeable is the higher I_1/I_3 ratios obtained for the n-6-n micelles compared to those reported by the probe in the presence of the n-2-n surfactants (Fig. 5). This can be attributed to the smaller micelles formed for the n-6-n surfactants than those by n-2-n series. For instance, aggregation numbers for 12-2-12 and 12-6-12 determined by time-resolved fluorescence quenching were respectively 114 [34] and 32 [35]. Besides, the formation of more hydrated aggregates is expected for n-6-n surfactants since the areas per surfactant molecule at the liquid/air interface for n-6-n are higher than those for n-2-n series. For instance the areas per surfactant molecule for 12-2-12 and 12-6-12 were estimated as 0.39 nm^2 and 1.85 nm^2, respectively [36]. Therefore for n-2-n series a tighter packing could take place due to intramolecular interactions between the hydrocabon chains. This could preclude the entrance of water molecules to the interior of micelles, which in turn would reflect in the smaller I_1/I_3 ratios as observed in Figure 5. The smaller I_1/I_3 ratios observed for n-2-n series are similar to those obtained for CTAB and DTAB (see Table 1) indicating that the packing for n-2-n and surroundings for this probe are similar to those of monomeric surfactants.

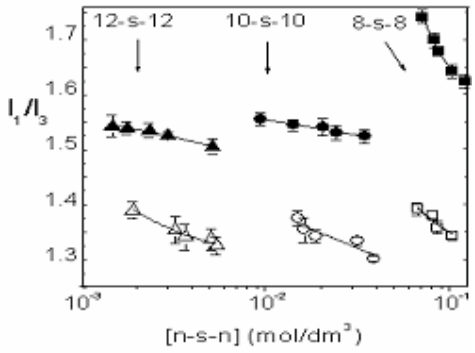

Figure 5. Variation of I_1/I_3 ratio for pyrene with surfactant concentration for n-2-n (open symbols) and n-6-n (filled symbols) at 25°C.

Conductimetric measurements.

Fig. 6 shows a representative plot of specific conductivity against concentration *C*, used to determine the CMC values and the respective ionization degrees (a) for all surfactants.

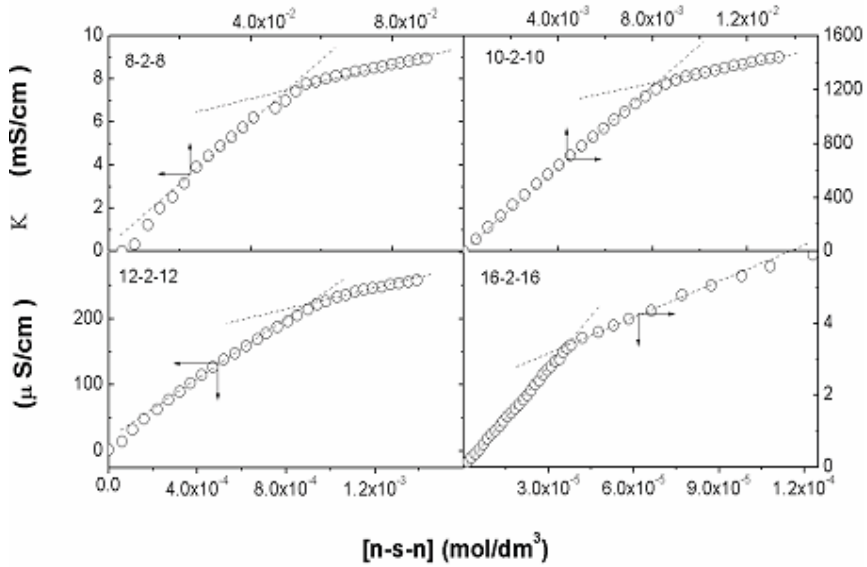

Figure 6. Conductimetric determination of the CMC for the n-2-n surfactants.

The table 1 shows that the CMC values for the n-2-n surfactants are smaller than those obtained for n-6-n series. Although the n-6-n series have four additional methylene groups when compared with n-2-n series they do not contribute to decrease the CMC as expected taking in account the higher hydrophobic character of these surfactants. The spacer containing six methylene groups is not long enough to fold into the interior, which in turn could explain the higher CMC values obtained for surfactants of the n-6-n series. The ionization degrees of the n-6-n surfactants are on average twice as high as those obtained by the n-2-n series (See Table 1). These results agree with those reported in the literature, which showed a significant increase in the micelle ionization degree upon increasing spacer carbon number for dimerics with a hydrophobic spacer: 10-*s*-10 [27- 29], 12-*s*-12 [18], 16-*s*-16 [30, 31]. In general the a values for

TABLE 1. Critical micellar concentrations (CMC), ionization degree (α), free energy of micellization (ΔG_M) and pyrene I_1/I_3 ratio for n-2-n and n-6-n surfactants in water

Surfactant	CMC* (mol/dm^3 ×10^{-3})	CMC** (mol/dm^3×10^{-3}) (*Literature*)	α	I_1/I_3 ratio for pyrene$^{\perp}$	ΔG_M*** (kJ/mol)
8-2-8	55	53	0.21	1.38	9.4
10-2-10	5.2	8.0	0.26	1.36	14.8
12-2-12	1.06	0.91 (0.84) [a]	0.30 (0.22[a]; 0.16 [c])	1.36	20.8
16-2-16	0.04	0.036(0.020) [b]	0.33(0.60[b])	1.30	29.3
8-6-8	51	60	0.48 (0.64[b])	1.65	7.1
10-6-10	6.0	9.1	0.43	1.54	12.5
12-6-12	1.00	1.1 (1.03) [c]	0.35 (0.33[b]; 0.20 [d])	1.53	19.4
16-6-16	0.03	0.05(0.043) [b]	0.50 (0.43[b])	1.55	24.5
C_8TAB[e]	-	290[e]	0.35[e]		5.06
C_{10}TAB	-	65	0.26	1.35	11.8
C_{12}TAB	-	14.6	0.25	1.36	18.4
C_{16}TAB	-	0.92	0.22	1.30	30.6

*PCA fluorescence ** Conductimetry; $^{\perp}$ [Surfactant] = 2x **CMC**; ***Values calculated using the equation $\Delta G = (0.5+\beta)RT \ln(CMC) - (RT/2)\ln 2$ and $\Delta G = RT(1.0+\beta)\ln(CMC)$ for dimeric and monomeric surfactants respectively(ref.4). [a] data taken from ref. 32; [b] data taken from ref. 39; [c] data taken from ref. 40; [d] data taken from ref. 41; [e] data taken from ref. 38;

both n-2-n and n-6-n series are higher than those reported for common alkyltrimethylammonium.

The free energies of micellization $\Delta G°$ were calculated using the equation DG= (0.5+ b)RT ln(CMC)-(RT/2)ln 2 and DG= RT(1.0+ b) ln(CMC) for dimeric and monomeric surfactants respectively. $\Delta G°$ was calculated by using the CMC and the α values determined from the conductivity measurements. A comparison between the $\Delta G°$ values obtained for monomeric and dimeric surfactants (Table 1) shows that the latter present nearly equal values to those obtained for the alkyltrimethylammonium bromides of same alkyl carbon number *m* . This equation yields as reported before [37], a free energy of transfer from water to the micellar pseudo-phase of 3.2± 0.3 kJ_mol per CH_2, a value close to that found for alkyltrimethylammonium bromides [37].

Conclusions

Two series of dimeric alkanediyl-α,ω-bis (dimethylalkylammonium bromide) n-2-n and n-6-n surfactants have been synthesized. For these dimeric surfactant micelles, the CMC values were determined using conductivity measurements and an extrinsic fluorescent probe, pyrenecarboxaldehyde. The ionization degrees for n-6-n and n-2-n micelles are in general higher than those reported for alkyltrimethylammonium bromides. From the measurements of pyrenecarboxaldehyde and ANS, the results indicated that in the submicellar range pre-aggregates may coexist with free monomers for all studied surfactants. Micropolarity studies using pyrene showed that the polarity inside the aggregates is influenced mainly by the spacer length and for n-6-n series the increase of alkyl carbon chain length decreases the amount of water contact in the aggregates. On the contrary, micropolarities reported for n-2-n surfactants series are similar to those obtained for DTAB and CTAB. Although fluorescence studies do not show much dependence on the alkyl length chain for 2-n-2 series, it may be possible that the pyrene molecules may not be sensing the aspects of hydration due to the tighter packing of the surfactant molecules in these micelles, especially if the probe is located deeper in the aggregates.

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