

Aggregation behavior of nonionic lactobionylamide-type gemini surfactants: steady-state and time-resolved fluorescence studies

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Nonionic gemini surfactants, N,N' -bisalkyl- N,N' -bis[(3-lactobionylamide)propyl]- α,ω -diaminoalkanes, have been synthesised with a great variety of structures differing by the length of the hydrophobic alkyl chains as well as the spacer group. Steady-state fluorescence quenching (SSFQ) and time-resolved fluorescence quenching (TRFQ) methods were employed in order to describe their aggregation phenomena on the basis of obtained micellar aggregation numbers (N_D) over the concentration range up to seventy-fold above the critical micelle concentration (cmc). The results suggest forming spherical micelles upon micellization and a slowly micelle growth with the surfactant concentration. The micelles formed by these structures have been also characterized in terms of the cmc and micropolarity due to the information provided by micelle-solubilized fluorescent probe.

1. INTRODUCTION

The ability of surfactants to self-associate into aggregates in solvent is perhaps the most fascinating aspect of amphiphilic species, and micelles description represents one of the central subjects for surface and colloid science studies [1]. Such parameters as size and shape of the surfactant ensembles as well as the micellar microenvironment characteristics are important due to developing materials that find utility in household and industrial applications [2]. A wide number of publications report on the self-assembly of small molecules into elongated aggregates such as rods, ribbons, helices, or tubules. In a case when these structures attain the sufficiently dimension i.e. became

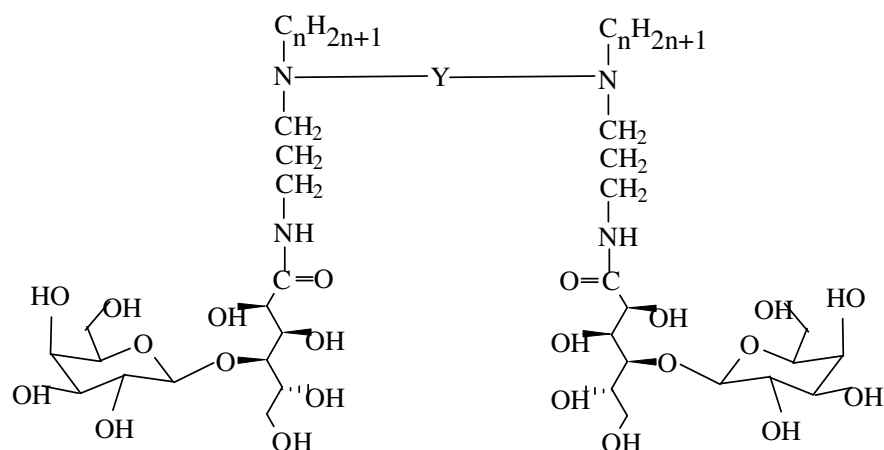
long and entangled enough, they are able to form gels entrapping the solvent molecules in a network [3,4]. The organization of the micellar associates is firmly connected with the architecture of the surfactant molecule [5]. Hence, for several decades, the relationship between the chemical structure of amphiphilic compounds and the morphology and physical properties of its assemblies in aqueous solutions has been the topic of intense experimental and theoretical work [6]. An exceptional attractive molecular geometry is presented by the gemini-type surfactants [6,7], which have been found to have a much stronger tendency for micellar growth and the formation of aggregates of lower curvature such as elongated, rod-like or thread-like micelles [8-10]. The morphology of the associates formed depends intimately as well on the carbon atoms number in the alkyl tails and polar headgroup type as on the nature and the length of the spacer in these surfactants [11].

Owing to our continuous efforts in developing new saccharide-derived self-assembling systems [12-18] we have now synthesized new gemini surfactants N,N' -bisalkyl- N,N' -bis[(3-lactobionylamide)propyl]- α,ω -diaminoalkanes where the spacer is differing in a number of methylene groups (for general formula and the abbreviations see Figure 1). In the present paper we present the fundamental characterization of the aggregation behavior and associates formed upon self-assembly of systems investigated. The micelle size were characterized by the micellar aggregation number, N , which is the number of surfactants making up a micelle and may be important in determining the stability and practical applications of the studied compounds. N is affected by different factors such as surfactant concentration, temperature, type and concentration of added electrolyte, organic additives [19], etc. Moreover, we refer also to the qualitative estimation of the penetrability of water molecules into the micellar structure, through the micropolarity of the micellar environment [20,21].

2. EXPERIMENTAL

2.1. Materials

The synthesis of $mbis(C_nGA)$ surfactants (see Figure 1) used in this study has been provided according to knowing methods described in [18]. All the reagents and solvents were the highest grade available commercially, dried, or freshly distilled as required. Pyrene was purchased from Molecular Probes, Inc. (Eubene, Or 97402) and cetylpyridinium chloride from Aldrich Chemical Co. (Milwaukee, WI). Water used for all experiments was doubly distilled and purified by means of a Millipore (Bedford, MA) Milli-Q purification system.



C_nH_{2n+1}	Y	Abbreviation
C_4H_9	$-CH_2CH_2-$	2bis(C_4LA)
$C_{10}H_{21}$	$-CH_2CH_2-$	2bis($C_{10}LA$)
C_4H_9	$-CH_2CH_2CH_2CH_2-$	4bis(C_4LA)
$C_{10}H_{21}$	$-CH_2CH_2CH_2CH_2-$	4bis($C_{10}LA$)
C_4H_9	$-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$	8bis($C_{10}LA$)
C_4H_9	$-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$	12bis($C_{10}LA$)

Fig. 1. Structures of the studied N,N' -bisalkyl- N,N' -bis[(3-lactobionylamide)-propyl]- α,ω -diaminoalkanes.

2.2. Methods

Fluorescence measurements were recorded on an IBH 5000U spectrometer, used as a single-photon sensitive spectrofluorimeter. The steady-state emission spectra were performed by means of an additional Model 5000U-06 steady-state accessory with xenon lamp. The fluorescence decays were recorded using the time-correlated with the hydrogen filled lamp. Emission and excitation slits were fixed at 16 nm. Measurements were performed in a thermostated 1cm^3 -cuvette holder at 20 and $60 \pm 0.5^\circ\text{C}$.

The critical micelle concentration (cmc) values of the gemini compound investigated were determined from the measurements of the pyrene polarity index, I_1/I_{III} , i.e. ratio of the intensities of the first and third vibronic peaks in the fluorescence emission spectra of pyrene [22,23]. From the plot of the I_1/I_{III} ratio vs. the surfactant concentration the cmc value were evaluated. The value of I_1/I_{III} at a concentration well above the cmc yielded information about the micropolarity of the solubilization site of the probe into the micelle [20,21].

Tab. 1. Characteristics of N,N'-bisalkyl-N,N'-bis[(3-lactobionylamide)propyl]- α,ω -diaminoalkanes.

Surfactant	Formula (Molecular weight)	Elemental analysis Found (Calcd)			¹ H NMR ^a
		C	H	N	
2bis(C ₄ LA)	C ₄₀ H ₇₈ O ₂₂ N ₄ (967.07)	49.59 (49.68)	8.01 (8.13)	5.84 (5.79)	0.85 (t, 6H, CH ₃ , J = 6.24Hz); 1.20–1.23 (m, 4H, CH ₃ CH ₂); 1.28–1.32 (m, 4H, N-CH ₂ CH ₂); 1.50–1.53 (m, 4H, CONHCH ₂ CH ₂ CH ₂ N); 2.33–2.37 (m, 8H, CH ₂ NCH ₂); 2.41 (s, 4H, NCH ₂ CH ₂ N); 3.00–3.06 (m, 4H, CONHCH ₂); 3.26–3.50 (m, CH, CH ₂ ,sugar); 3.67–5.10 (m, OH, sugar); 4.45 (d, 2H, CH-acetal, J = 7.2 Hz); 7.57 (t, 2H, CONH)
2bis(C ₁₀ LA)	C ₅₂ H ₁₀₂ O ₂₂ N ₄ (1135.39)	55.16 (55.01)	9.11 (9.06)	4.88 (4.94)	0.83 (t, 6H, CH ₃ , J = 6.24Hz); 1.20–1.24 (m, 28H, CH ₃ (CH ₂) ₇); 1.29–1.34 (m, 4H, N-CH ₂ CH ₂ (CH ₂) ₇); 1.48–1.52 (m, 4H, CONHCH ₂ CH ₂ CH ₂ N); 2.32–2.35 (m, 8H, CH ₂ NCH ₂); 2.39 (s, 4H, NCH ₂ CH ₂ N); 3.00–3.09 (m, 4H, CONHCH ₂); 3.20–3.50 (m, CH, CH ₂ ,sugar); 3.59–5.11 (m, OH, sugar); 4.50 (d, 2H, CH-acetal, J = 7.2 Hz); 7.56 (t, 2H, CONH)
4bis(C ₄ LA)	C ₄₂ H ₈₂ O ₂₂ N ₄ (995.12)	50.77 (50.69)	8.20 (8.30)	5.58 (5.63)	0.84 (t, 6H, CH ₃ , J = 6.24Hz); 1.19–1.21 (m, 4H, CH ₃ CH ₂); 1.29–1.35 (m, 8H, N-CH ₂ CH ₂); 1.49–1.52 (m, 4H, CONHCH ₂ CH ₂ CH ₂ N); 2.33–2.37 (m, 12H, CH ₂ N(CH ₂)CH ₂); 3.01–3.09 (m, 4H, CONHCH ₂); 3.29–3.53 (m, CH, CH ₂ ,sugar); 3.65–5.08 (m, OH, sugar); 4.49 (d, 2H, CH-acetal, J = 7.2 Hz); 7.54 (t, 2H, CONH)
4bis(C ₁₀ LA)	C ₅₄ H ₁₀₆ O ₂₂ N ₄ (1163.44)	55.84 (55.75)	9.22 (9.18)	4.87 (4.82)	0.85 (t, 6H, CH ₃ , J = 6.24Hz); 1.21–1.26 (m, 28H, CH ₃ (CH ₂) ₇); 1.27–1.33 (m, 8H, N-CH ₂ CH ₂ (CH ₂) ₇); 1.48–1.53 (m, 4H, CONHCH ₂ CH ₂ CH ₂ N); 2.29–2.34 (m, 12H, CH ₂ N(CH ₂)CH ₂); 3.04–3.10 (m, 4H, CONHCH ₂); 3.21–3.53 (m, CH, CH ₂ ,sugar); 3.57–5.13 (m, OH, sugar); 4.52 (d, 2H, CH-acetal, J = 7.2 Hz); 7.54 (t, 2H, CONH)
8bis(C ₄ LA)	C ₄₆ H ₉₀ O ₂₂ N ₄ (1051.23)	52.49 (52.56)	8.69 (8.63)	5.27 (5.33)	0.82 (t, 6H, CH ₃ , J = 6.24Hz); 1.20–1.24 (m, 4H, CH ₃ CH ₂ and 8H, CH ₂ (CH ₂) ₄ CH ₂); 1.30–1.35 (m, 8H, N-CH ₂ CH ₂); 1.50–1.53 (m, 4H, CONHCH ₂ CH ₂ CH ₂ N); 2.33–2.37 (m, 12H, CH ₂ N(CH ₂)CH ₂); 3.01–3.09 (m, 4H, CONHCH ₂); 3.29–3.53 (m, CH, CH ₂ ,sugar); 3.65–5.08 (m, OH, sugar); 4.49 (d, 2H, CH-acetal, J = 7.2 Hz); 7.54 (t, 2H, CONH)
12bis(C ₄ LA)	C ₅₀ H ₉₈ O ₂₂ N ₄ (1107.33)	54.17 (54.23)	8.89 (8.92)	5.14 (5.06)	0.85 (t, 6H, CH ₃ , J = 6.24Hz); 1.20–1.27 (m, 4H, CH ₃ CH ₂ and 16H, CH ₂ (CH ₂) ₈ CH ₂); 1.28–1.34 (m, 8H, N-CH ₂ CH ₂); 1.51–1.53 (m, 4H, CONHCH ₂ CH ₂ CH ₂ N); 2.32–2.35 (m, 12H, CH ₂ N(CH ₂)CH ₂); 3.00–3.07 (m, 4H, CONHCH ₂); 3.31–3.52 (m, CH, CH ₂ ,sugar); 3.78–5.11 (m, OH, sugar); 4.51 (d, 2H, CH-acetal, J = 7.2 Hz); 7.52 (t, 2H, CONH)

The fluorescence decay curves were fitted to the equation described by Alargova *et al.* [19] yielding the average aggregation number, N_D . The time-resolved fluorescence quenching (TRFQ) measurements were carried out using pyrene as the fluorescence probe and cetylpyridinium ion as the fluorescence quencher. In all these experiments the probe concentration, [P], was kept at low level, such that $[P]/[\text{micelle}] < 0.05$. The molar concentration ratio $[Q]/[\text{micelle}]$ was adjusted as to be close to 1 – it was varied between 0 and 1.5 [19].

3. RESULTS AND DISCUSSION

A new class of amphiphiles, so called gemini surfactants, is currently raising much interest in the scientific literature [22]. The designed gemini structures are made up of two amphiphilic moieties comprising two lactobionamide-derived head groups and they are connected by the methylene spacer of various length. Generally, in the literature the cationic dimeric compounds are extensively investigated by means of fluorescence methods due to their aggregation phenomena [24,25]. Paddon-Jones *et al.* [22] reported on the micellization behavior of nonionic dimeric structures of the dimethylene 1,2-bis(*N*-polyethyleneglycol dodecylamide) type. The experiments have been carried out by means of pyrene fluorescence probing and time-resolved fluorescence quenching. The sugar-derived gemini surfactants appeared in SANS [11] as well as electron microscopy studies [26] and they are found to display remarkable properties including the formation of thread-like micelles and giant vesicles. In the case of *N,N'*-bisalkyl-*N,N'*-bis[(3-aldonylamide)propyl] ethylenediamines [18] the applied steady-state fluorescence measurements showed that they can form micelles at an exceptionally low concentration. The present contribution deals with the application of fluorescence methods in the aggregation studies of lactobionamide-derived gemini compounds with varying both the hydrophobic tail, and spacer length.

3.1. Steady-state fluorescence measurements

Steady-state fluorescence measurements were performed for the critical micelle concentration and microenvironment polarity evaluation. Figure 1 presents variations of the studied surfactants concentration vs. the observed I_I/I_{III} ratios in the fluorescence emission spectra of pyrene. It is well known that the intensities of the first (I_I) and the third (I_{III}) vibronic peaks of pyrene are highly sensitive on the polar nature of medium surrounding [20,21]. The plots show rather broad breaks related to critical micelle concentration. According to Paddon-Jones *et al.* interpretation [22], we take as cmc the value of

concentration corresponding to the midpoint of the decrease of I_I/I_{III} ratio. The obtained cmc (Tab. 2) of the studied $mbis(C_nLA)$ s achieves low values between 7.11×10^{-5} and $5.98 \times 10^{-4} M$ for $2bis(C_{10}LA)$ and $4bis(C_4LA)$, respectively. The results show that for the series of $mbis(C_4LA)$ cmc at first increases with increase in the number of carbon atom in the spacer from 2 to 4 and then decreases achieving the lower value for $12bis(C_4LA)$. The similar dependence was observed also for cationic dimeric surfactant of N,N -bis(alkyldimethyl)- α,ω -alkane diammonium dibromides [24]. In our previous paper we have reported on the N,N -bisalkyl- N,N -bis[(3-aldonylamide)propyl]ethylene-diamines dimeric family (referred as $bis(C_nX)$, where X =gluconamide, glucoheptonamide or lactobionamide moiety) [18] and for the n -dodecyl derivatives we have observed micellization process at the concentrations between 3.79×10^{-6} and $8.91 \times 10^{-6} M$, depending on the polar headgroup kind. Thus, the new gemini compound with n -decyl alkyl chain forms micelles at higher concentration than mentioned above bisaldonylamide-type amphiphiles. However, the obtained value for $2bis(C_{10}LA)$ is in an agreement with nonionic dimeric structure dimethylene-1,2-bis(N -hexaethyleneglycol dodecylamide) (referred as $(C_{12}AmEG6)_2$: $cmc=1.9 \times 10^{-5} M$) [22]. The n -dodecyl dicerphalic saccharide-derivatives show the cmc data in the range of 2.51×10^{-4} to $7.94 \times 10^{-4} M$, which is of the same magnitude as for the studied dimeric compounds [14]. It was found that the evaluated cmc value for $mbis(C_nLA)$ is similar to the single-tail, single-head sugar-based nonionics containing n -dodecyl tail (e.g. 1.46×10^{-4} to $2.49 \times 10^{-4} M$ for N -dodecyl- N -methylaldonamides [27], $1.9 \times 10^{-4} M$ for n -dodecylglucoside [28], and $2.3 \times 10^{-4} M$ for n -dodecyl-2-amino-2-deoxy- β -D-glucopyranoside ($C_{12}GluNH_2$) [29]).

The second part deals with microenvironment characteristics. Some authors [30] suggest that the first few methylene groups in the hydrocarbon tail lying near to the polar headgroup may be in contact with water. Thus, water molecules may somehow penetrate into the hydrophobic core of micelles. The obtained II/III ratios from 1.680 to 1.694 (for water $II/III=1.87$) indicate a considerable higher polarity sensed by pyrene (see Tab. 2) in respect to, for instance, nonionic gemini $(C_{12}AmEG6)_2$ ($II/III=1.25$) [22] and for single-tail, single-head sugar-based n -octyl- β -D-glucopyranoside (referred as OBG: $II/III=1.01$ for $[OBG]=29.0 \times 10^{-3} mol/kg$, i.e. $[OBG]=1.1 \times cmc_{OBG}$, and $II/III=1.05$ for $[OBG]=55.4 \times 10^{-3} mol/kg$, i.e. $[OBG]=2.1 \times cmc_{OBG}$) [21]. This indicates forming of more water imbued structure in case of studied gemini lactobionylamide-type surfactants.

Tab. 2. Aggregation parameters of N,N'-bisalkyl-N,N'-bis[(3-lactobionylamide)propyl]- α,ω -diaminoalkanes by means of fluorescence techniques at the temperature 20°C.

System studied	Steady-State Fluorescence Measurements		Time-Resolved Fluorescence Quenching Measurements				
	cmc (M)	(I_I/I_{III}) $_{C \gg cmc}$	$\times cmc$	$\tau = A_2^{-1}$ (ns)	k_q ($10^7 s^{-1}$)	N_D	Nk_q ($10^7 s^{-1}$)
2bis(C ₄ LA)	2.57×10 ⁻⁴	1.689	10	275	2.19	18.3	40.1
			30	280	2.01	20.2	40.7
			50	283	1.74	23.5	40.8
			70	287	1.64	25.0	41.0
2bis(C ₁₀ LA)	7.11×10 ⁻⁵	1.685	10	319	1.67	27.4	45.8
			30	323	1.56	29.4	46.0
			50	324	1.43	32.3	46.1
			70	328	1.29	35.7	46.2
4bis(C ₄ LA)	5.98×10 ⁻⁴	1.694	10	284	1.98	17.5	34.7
			30	289	1.82	19.1	34.8
			50	290	1.66	21.1	35.0
			70	293	1.45	24.2	35.1
4bis(C ₁₀ LA)	1.03×10 ⁻⁴	1.690	10	324	1.86	26.6	49.5
			30	326	1.70	29.3	49.8
			50	329	1.60	31.2	50.0
			70	373	1.45	34.5	50.1
8bis(C ₄ LA)	3.48×10 ⁻⁴	1.684	10	289	1.98	21.0	41.5
			30	292	1.80	23.2	41.8
			50	296	1.59	26.4	42.0
			70	299	1.41	29.7	42.0
12bis(C ₄ LA)	9.76×10 ⁻⁵	1.680	10	293	1.85	24.2	44.7
			30	295	1.70	26.4	45.0
			50	298	1.68	27.0	45.3
			70	302	1.47	30.8	45.4

3.2. Time-resolved fluorescence quenching measurements

To determine micellar aggregation numbers of $m\text{bis}(\text{C}_n\text{LA})$'s the time-resolved fluorescence decay were recorded. Fluorescence quenching methods are among the most reliable for the micellar aggregation numbers estimation. They take advantage of the quenching process of emission from fluorescence probe by a quencher added to a solution containing a known amount of surfactant and probe [25,31,32].

Fluorescence Decay Studies. We started the TRFQ experiments on $m\text{bis}(\text{C}_n\text{LA})$ solutions of various surfactant concentrations containing pyrene as a fluorescence probe and no quenching agent. Each decay curve for different sets of experimental parameters (i.e. type of surfactant, its concentration in aqueous solution, quencher concentration) was analyzed separately to yield the fitting parameters.

Fluorescence Lifetime and Rate Constant of Intramicellar Quenching. In the case of free-quencher samples the fluorescence emission intensity decays following the exponential law, the decay time being the probe lifetime. The values of the lifetimes (see Tab. 2) in the systems studied agree quite well, indicating that probe is fully attached to micelles, within the experimental error. The parameter A_2 (which is equal to reciprocal of the lifetime value) exhibits slightly surfactant and quencher concentration dependence. The series of decay curves obtained for the samples with various quencher amounts is shown in Figure 3a. The rate constant for the intramicellar quenching of pyrene by the cethylpyridinium ion, k_q , carries information about the size distribution of the micelles [33]. However, k_q is slightly dependent on quencher concentration, indicating polydispersity of the formed aggregates [34].

Aggregation Numbers. The analysis of the each obtained fluorescence decay curves individually yields the necessary fitting parameters that enable calculation of micellar aggregation numbers. Tab. 2 summarises the results obtained for all investigated lactobionamide-type gemini structures. We observed that the number of the gemini molecules per micelle tends to increase slightly with increasing of the surfactant concentration in the concentration range from 10 to $70 \times \text{cmc}_i$ (i – a given compound). The results for $2\text{bis}(\text{C}_4\text{LA})$ at low concentrations reveal the N_D values of 18 and increases to 25 due to the increase of the aggregate size. For $2\text{bis}(\text{C}_{10}\text{LA})$ we observed the objects containing from 27 to 35 molecules. The series of typical decay curves obtained for the different surfactant concentration is shown in Figure 3b.

For the surfactants investigated, the values of Nk_q is constant and equal to $(4.24 \pm 0.77) \times 10^6 \text{s}^{-1}$ (for comparison it is equal to $3.2 \pm 0.8) \times 10^6 \text{s}^{-1}$ for cationic gemini compound of ethanediyl-1,2-bisdodecyldimethylammonium bromide type [25]), irrespective of surfactant concentration. Such behavior is expected for spherical or slightly elongated micelles [25,35].

No information about the aggregation behavior of sugar-derived gemini compounds comprising *n*-butyl chains are available in the literature. The *mbis*(C_{*n*}LA) aggregation numbers are from 17 to 24 and from 26 to 27 gemini molecules per micelle, for *n*-butyl and *n*-decyl derivatives, respectively, at surfactant concentration equal to ten times of their cmc values. If one calculates the number of hydrophobic chains in each micelle it yield from 34 to 48 *n*-butyl tails and from 52 to 54 *n*-decyl tails, and it is in good agreement to the respective literature values for *n*-octyl single-head single-tail amphiphilic derivatives. Thus, the light scattering measurements gave the data for obtaining C₈GluNH₂ micellar aggregation number of 41 to 43 at the different temperatures [29], and for an *N*-octylamino-1-deoxylactitol studied by Rico-Lattes et al. it was obtained $N=34.2$ [36]. However, *n*-octyl- β -D-glucopyranoside form aggregates containing 54 surfactant molecules at very low micellar concentration (near above the cmc value) [21]. Similarly, for *n*-octyl- β -glucoside (denoted as OBG) [37] Giordano *et al.* presented an aggregation number of 66 at low concentration, and it increases to 76 for higher concentration due to the increase of the size of the micelles.

4. CONCLUDING REMARKS

For all compounds studied we observed a slightly concentration dependent micellar growth. The obtained aggregation numbers correspond to the values expected for the spherical objects formed upon micellization in the concentration range investigated. The remark that N_D goes up with alkyl chain length for the 2*bis*(C_{*n*}LA) and 4*bis*(C_{*n*}LA) is in an agreement with those presented in literature [18,22]. This tendency is explained on the basis of the theory that the radius of a spherical micelle (it is taken to be approximately equal to the length of the fully stretched alkyl chain) increases with the number of carbon atoms as a result of which the volume of the micelle is increased. Although the spherical micelle are observed for the concentration near above the cmc they are rather less probable for *mbis*(C_{*n*}LA)s due to geometrical reasons, which suggest an assuming that they probably form a cylindrical or rod-like micelle at the higher concentrations. Therefore, the experiments are actually carried out at much higher concentrations than their cmc values, where practically only one type of micelles is present. In such a model an increase in the length of the hydrophobic tail would also increase the volume of the micelle.

When one takes into account the series of *mbis*(C₄LA) the effect of the hydrocarbon chain linking the two nitrogen atoms on the aggregation phenomena is significant. When the value of *m* rises from 2 to 12 the spacer becomes more flexible. On the other hand, increase in the length of the alkyl

chain linking the two amphiphilic moieties is accompanied by increase in its hydrophobicity. It is reflected also in decrease in the cmc values for the structures comprising longer spacers. The hydrophobic nature and flexibility of longer spacers induces differences in the formed aggregates shape according to the tendency of entering itself inside the micelle in order to minimize its contact with water. Thus the micelle interior is denser as compared to those formed by compounds with shorter spacers and the effective volume inside their assemblies is therefore considerably reduced.

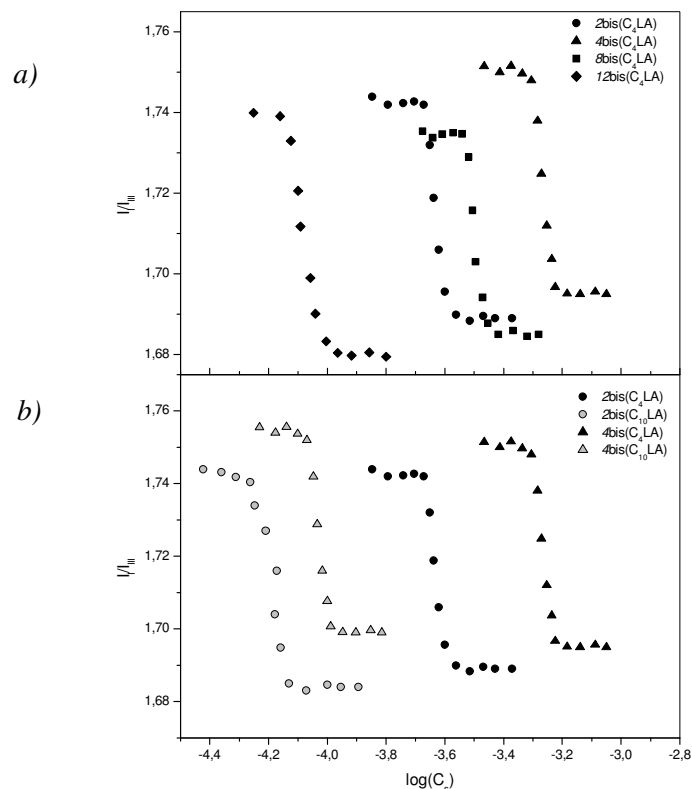


Fig. 2. Variation of pyrene polarity ratio I_I/I_{III} with the surfactant concentration for a) $m\text{bis}(C_4\text{LA})$, where $m=2, 4, 8, 10$ and b) $2\text{bis}(C_4\text{LA})$, $2\text{bis}(C_{10}\text{LA})$, $4\text{bis}(C_4\text{LA})$, and $4\text{bis}(C_{10}\text{LA})$ at 20°C .

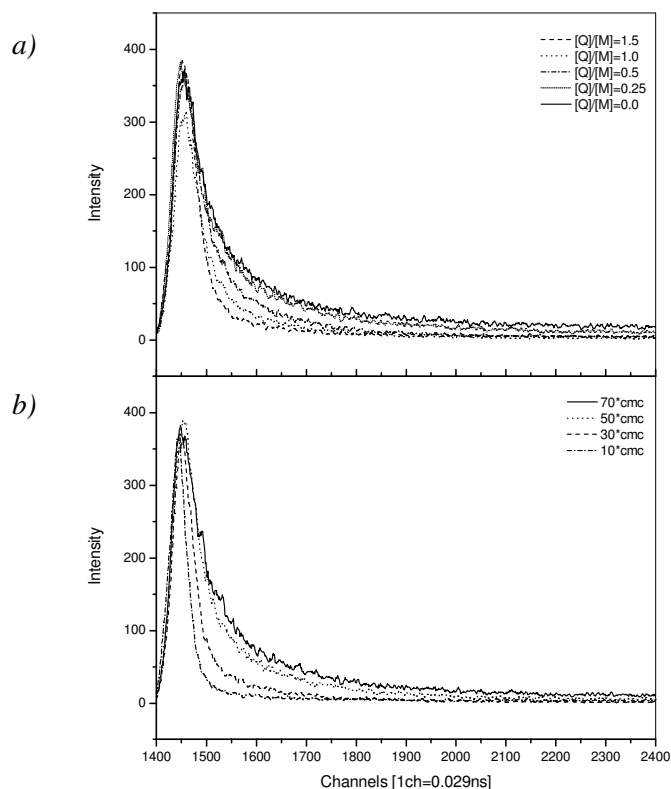


Fig. 3. Typical fluorescence decay curves a) for 10mM 2bis(C₄LA) solution at different quencher-to-micelle ratios ($[Q]/[M]$), and b) as a function of surfactant concentration without quencher at the temperature 20°C.

Independently on the tails and spacer length are the polar headgroups appreciable hydrated due to the presence of the numerous hydroxyl groups in the lactobionylamide moieties. Thus, the hydrophilic region of aggregates formed consists of the sugar-derived entity and entrapped water molecules, which is additionally proved by the high values of micropolarity obtained by fluorescence method.

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REFERENCES

- [1] Hansson P., Jönsson B., Ström C., Söderman O., *J. Phys. Chem. B* 104, 3496 (2000).
- [2] Grieser F., Drummond C.J., *J. Phys. Chem.* 92, 5580 (1988).
- [3] Fuhrhop J.-H., Helfrich W., *Chem. Rev.* 93, 1565 (1993)
- [4] Oda R., Huc I., Candau S.J., *Angew. Chem. Int. Ed.* 37, 2689 (1998).
- [5] Bulavin L.A., Garamus V.M., Ostanevich Yu.M., *Colloid Surfaces A* 94, 53 (1995).
- [6] Menger F.M., Littau C.A., *J. Am. Chem. Soc.*, 115, 10083 (1993).
- [7] Zana R., Benrraou M., Rueff R., *Langmuir* 7, 1072 (1991).
- [8] Oda R., Huc I., Homo J.-C., Heinrich B., Schmutz M., Candau S.J., *Langmuir* 15, 2384 (1999).
- [9] Bernheim-Groswasser A., Zana R., Talmon Y., *J. Phys. Chem. B* 104, 4005 (2000).
- [10] Oda R., Huc I., Candau S.J., *Chem. Commun.* 2105 (1997).
- [11] De S., Aswal V.K., Goyal P.S., Bhattacharya S., *J. Phys. Chem. B* 102, 6152 (1998).
- [12] Burczyk B., Syper L., Wilk K.A., *Polish Appl. Patent P.* 331294 (1999).
- [13] Syper L., Wilk K.A., Sokołowski A., Burczyk B., *Progr. Colloid Polym. Sci.* 110, 199 (1998).
- [14] Wilk K.A., Syper L., Burczyk B., Sokołowski A., Domagalska B.W., *J. Surfact. Deterg.* 3, 185 (2000).
- [15] Maliszewska I., Wilk K.A., Burczyk B., Syper L., *Progr. Colloid Polym. Sci.* 118, 172 (2001).
- [16] Wilk K.A., Syper L., Burczyk B., Maliszewska I., Jon M.J., Domagalska B.W., *J. Surfact. Deterg.* 4, 155 (2001).
- [17] Wilk K.A., Syper L., Domagalska B.W., Komorek U., Maliszewska I., Gancarz R., *J. Surf. Deterg.* 5, 235 (2002).
- [18] Komorek U., Wilk K.A., *J. Colloid Interface Sci.*, in press.
- [19] Alargova R.G., Kochijashky I.I., Sierra M.L., Zana R., *Langmuir* 14, 5412 (1998).
- [20] Kalyanasundaram K., Thomas J.K., *J. Am. Chem. Soc.* 99, 2039 (1977).
- [21] Pastor O., Junquera E., Aicart E., *Langmuir* 14, 2950 (1998).
- [22] Paddon-Jones G., Regimond S., Kwetkat K., Zana R., *J. Colloid Interface Sci.* 243, 496 (2001).
- [23] Dong D.C., Winnik M.A., *Photochem. Photobiol.* 35, 17 (1982).
- [24] Devinsky F., Lacko I., Imam T., *J. Colloid Interface Sci.* 143, 336 (1991).
- [25] Danino D., Talmon Y., Zana R., *Langmuir* 11, 1448 (1995).
- [26] van Doren H.A., Smits E., Pestman J.M., Engberts J.B.N.F., Kellog R.M., *Chem. Soc. Rev.* 29, 183 (2000).
- [27] Burczyk B., Wilk K.A., Sokołowski A., Syper L., *J. Colloid Interface Sci.* 240, 552 (2001).
- [28] Retailleu L., Laplace A., Fensterbank H., Larpent C., *J. Org. Chem.* 63, 608 (1998).
- [29] Boullanger P., Chevalier Y., *Langmuir* 12, 1771 (1996).
- [30] Varela A.S., Macho M.I.S., Gonzales A.G., *Colloid Polym. Sci.* 273, 876 (1995) and references therein.
- [31] Fraiji L.K., Hayes D.M., Werner T.C., *J. Chem. Edu.* 69, 424 (1992).
- [32] Vasilescu M., Anghel D.F., Almgren M., Hansson P., Saito S., *Langmuir* 13, 6951 (1997).
- [33] von Berlepsch H., Stähler K., Zana R., *Langmuir* 12, 5033 (1996).
- [34] Bales B.L., Ranganathan R., Griffiths P.C., *J. Phys. Chem. B* 105, 7465 (2001).
- [35] Van der Auweraer M., De Schryver F.C., *Chem. Phys.* 111, 105 (1987).
- [36] Rico-Lattes I., Lattes A., *Colloids Surfaces A.* 123-124, 37 (1997).
- [37] Giordano R., Maisano G., Teixeira J., *J. Appl. Cryst.* 30, 761 (1997).

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