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Micelles in Mixtures of Sodium Dodecyl Sulfate and a Bolaform Surfactant

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Mixtures composed of water, sodium dodecyl sulfate (SDS), and a bolaform surfactant with two aza-crown ethers as polar headgroups (termed Bola C-16) were investigated by modulating the mole ratios between the components. The two surfactants have ionic and nonionic, but ionizable, headgroups, respectively. The ionization is due to the complexation of alkali ions by the aza-crown ether unit(s). Structural, thermodynamic, and transport properties of the above mixtures were investigated. Results from surface tension, translational self-diffusion, and small angle neutron scattering (SANS) are reported and discussed. Interactions between the two surfactants to form mixed micelles result in a combination of electrostatic and hydrophobic contributions. These effects are reflected in the size and shape of the aggregates as well as in transport properties. The translational diffusion of the components in mixed micelles, in particular, depends on the Bola C-16/SDS mole ratio. Nonideality of mixing of the two components was inferred from the dependence of the critical micelle concentration, cmc, on the mole fraction of Bola C-16. This behavior is also reflected in surface adsorption and in the area per polar headgroup at the air−water interface. SANS data analysis for the pure components gives results in good agreement with previous findings. An analysis of data relative to mixed systems allows us to compute some structural parameters of the mixed aggregates. The dependence of aggregation numbers, ν_T, on the Bola C-16/SDS mole ratio displays a maximum that depends on the overall surfactant content and is rationalized in terms of the nonideality of mixing. Aggregates grow perpendicularly to the major rotation axis, as formerly observed in the Bola C-16 system, and become progressively ellipsoidal in shape.

Introduction

The supramolecular association of surfactant molecules into micelles, vesicles, and other supramolecular entities is the result of a complex balance between different contributions, controlling the overall system stability.[1−3] Efforts to tune the aggregate size and shape require the modulation of hydrophobic, surface tension, and electrostatic terms.[4,5] The best strategy to modulate such effects is making use of surfactant mixtures. For instance, mixing cationic and anionic surface-active agents gives rise to the formation of rods, vesicles, or precipitates, depending on the relative amounts of the component(s).[6] Significant results along this line can also be obtained by mixing ionic and nonionic
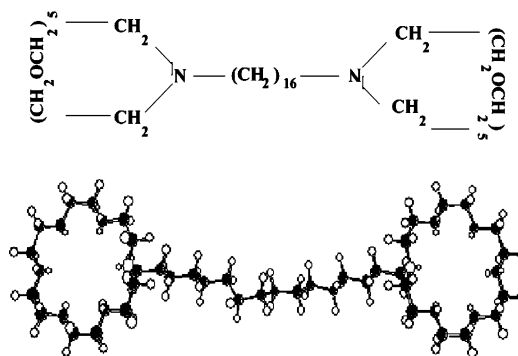

Figure 1. Schematic stereochemical view of the Bola C-16 molecule. The 2-D structure of the aforementioned molecule is also reported.

surfactants and/or modifying the net charge of the mixed aggregates by increasing the medium ionic strength, by changing the pH, and so forth.[7−9]

It was recently observed that it is possible to modulate the size and the shape of micellar aggregates formed by a nonionic, but ionizable, bolaform surfactant.[10] The chemical structure of this

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species, reported in Figure 1, consists of two aza-crown ether units covalently linked to both sides of a hexadecyl chain. Each aza-crown ether group in the above surfactant species, hereafter termed Bola C-16, is selective with respect to sodium ions and protons.[11,12] The molecular structure and some properties of Bola C-16 have been reported.[10,13] The presence of sodium ions or modifications of the pH of the medium are concomitant with changes in micelle size and in the area per polar headgroup.[10]

Significant changes in both the size and shape of Bola C-16 micelles may also presumably occur by adding sodium-based anionic surfactants. The uptake of alkyl chains into the aggregates gives rise to mixed micelles, and as a result of significant sodium ion uptake in the aza-crown unit, modification of the state of charge and of the packing of the self-associated species is expected. Such behavior may influence the electrostatic interactions occurring between the anionic groups and the polar head(s) of Bola C-16, located in the Stern layer of micelles. Bola C-16 becomes ionic upon binding significant numbers of sodium ions. The size and shape of the mixed micelles are, presumably, sensitive to such effects.

Apart from fundamental interest in such systems, there are potential applications of these mixtures in saline media, essentially in the selective uptake of ions from the solvent and in the stabilization of the resulting mixed aggregates. Biochemical applications can also be important because aza-crown ethers and their alkyl derivatives are used in ion transport through biological membranes.[14,15]

To shed light on some aspects of the binary surfactant mixture formed by Bola C-16 and SDS, structural, thermodynamic, and transport properties in the dilute aqueous regime were investigated. Even though it gives evidence of the occurrence of significant solute−solute interactions, thermodynamics does not give direct information on the molecular packing of the two surfactants when they form mixed aggregates. To characterize in more detail the size and shape of the aggregates, pulsed field gradient spin−echo NMR (PGSE NMR) and small angle neutron scattering (SANS) measurements were used.

Experimental Section

Materials. Bola C-16 was obtained by reacting 1,4,7,10,13-pentaoxa-16-azacyclo-octadecane (indicated as *N*-aza-18-crown-6) and α−ω hexadecane-dioic acid. The aza-crown ether (Aldrich) was used as received. The dicarboxylic acid (Sigma-Aldrich) was reacted with $SOCl_2$, transformed into a diacyl chloride, and mixed with the aza-crown ether in the presence of $N(C_2H_5)_3$ as a buffer. Residual CO groups were reduced by $LiAlH_4$. The product was washed in 0.1 M HCl, in aqueous Na_2CO_3, in dichloromethane, and in dichloromethane−methanol and finally was vacuum dried. ^{1}H NMR and elemental analysis confirmed the product purity. Some physicochemical properties of Bola C-16 and more synthetic details are reported elsewhere.[12,13]

SDS, from Sigma-Aldrich, was purified by dissolution in hot ethanol, filtered, and precipitated with acetone. The whole procedure was repeated twice, and the precipitate was vacuum dried. The product purity was confirmed by measuring the cmc of the surfactant at 25.00 ± 0.01 °C. Equivalent conductivity results are nearly superimposable with previous data.[16]
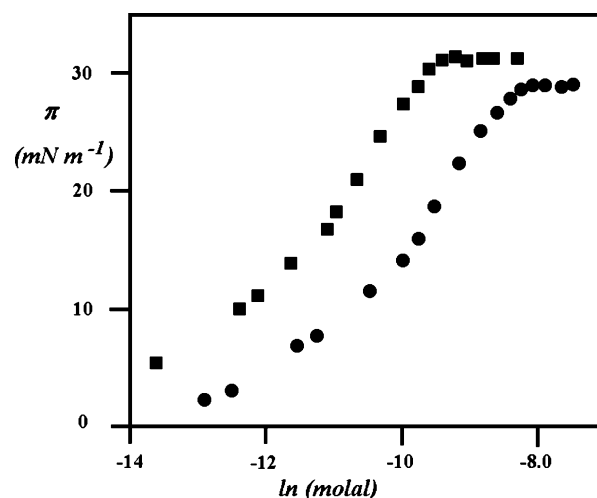

Figure 2. Surface pressure, π (mN m^{-1}), of some water/Bola C-16/SDS mixtures as a function of the overall surfactant content, in logarithmic form, at 25.0 °C. Data refer to 0.347 Bola C-16 (■) and 0.116 Bola C-16 (●) mole fractions.

The purity of both surfactants was confirmed by the absence of minima in surface tension versus log(c) plots close to the cmc.[17]

Water was deionized and doubly distilled over alkaline $KMnO_4$. Its conductivity, χ, is close to 1 μS cm^{-1} at 25.0 ± 0.1 °C. When required, water was replaced by D_2O, Merck 99.8 atom % isotopic enrichment. The solutions were prepared by weight.

Methods. *NMR Self-Diffusion.* Measurements were performed by pulsed field gradient spin−echo (PFG-SE NMR) on a WM 300 unit (Bruker, Cambridge, MA). The field gradient width, δ, is between 2 and 7 ms, and its duration, Δ, is 250 ms. The field gradient strength, G, is 6.3 G cm^{-1}, and the number of transients is 16 or 32. The NMR unit is equilibrated at 25.0 ± 0.2 °C with a thermostat. More details on the apparatus setup and NMR pulse sequences are given elsewhere.[18,19] In dilute regimes, the line widths are narrow, and the self-diffusion values are accurate.[20] The errors in such values are up to ±2%.

Measurements were performed on HDO (for water), methyl (the end group of SDS), and oxyethylene protons for Bola C-16. Within the experimental data accuracy, NMR self-diffusion values, D_{NMR}, relative to SDS (the CH_3 resonance lines) and Bola C-16 oxyethylene (OC_2H_4O) signals in mixed micelles are equivalent.

Surface Tension. A Kruss unit (model 333) measured the surface tension, σ, to an accuracy of ±0.1 mN m^{-1}. The solutions are located in a vessel at 25.00 ± 0.05 °C. The platinum Du Noüy ring was flame cleaned and washed with 1 M HCl and several times with doubly distilled water. Distilled water ($\sigma = 72.1$ mN m^{-1} at 25 °C)[21] and absolute ethanol ($\sigma = 21.8$ mN m^{-1} at 25 °C)[22] were used to calibrate the instrument.

Known amounts of Bola C-16, SDS, or Bola C-16/SDS mixtures were added to the solvent by a weight buret. The mixtures were equilibrated for 20 min to minimize adsorption kinetics effects. The surface tension data reported in Figure 2 are the mean values of many independent measurements. The uncertainty of individual π values ($\pi = \sigma° - \sigma$) is ±0.2 mN m^{-1}.

Small Angle Neutron Scattering. Measurements were performed at the Rutherford Appleton Laboratory on the ISIS pulsed neutron source, Didcot (Oxford), U.K., by using the time-of-flight SANS

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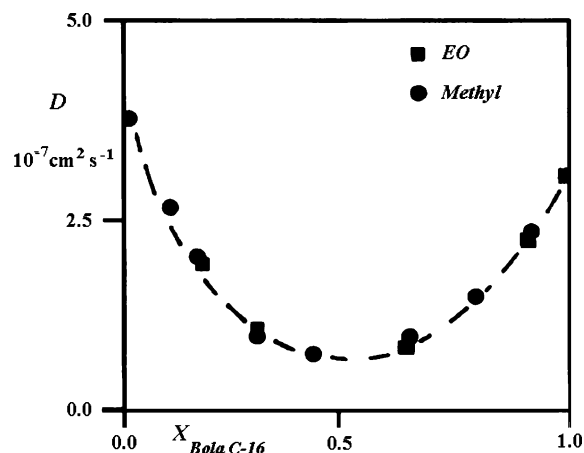(22) Korosi, G.; Kovàts, E. *J. Chem. Eng. Data* **1981**, *26*, 323−332.

Figure 3. Collective self-diffusion coefficient of micelles, D_{NMR}, in 10^{-7} cm^2 s^{-1}, as a function of the Bola C-16 mole fraction, X_{Bola}, in the mixture at 25.0 °C. The overall surfactant content is 40.0 mmol kg^{-1}. Values relative to the EO groups (■) and methyl groups (●) are reported.

instrument LOQ.[23] The samples were contained in fused silica cells of 2 mm path length and placed 4.3 m from the main two-dimensional detector. The temperature was kept at 25.0 ± 0.2 °C by an external oil bath. Data from the main detector were averaged around annular rings before correction for transmission, detector efficiency, and monitor response.[24] The sample transmission was corrected for the wavelength dependence. Simultaneous neutron diffraction data were combined in the wavelength range of 2−10 Å to give net intensities in the Q range (the scattering vector, Q, is sin $(4\pi/\lambda)$, where 2θ is the scattering angle) between 0.01 and 0.23 Å^{-1}. The net intensities were converted to absolute differential scattering cross sections per unit sample volume, $d\Sigma(Q)/d\Omega$ (in cm^{-1}), after comparison with precalibrated secondary standards.[25,26]

Scattering from the solvent blank was subtracted from that of the samples. More details are reported elsewhere.[23]

Results and Discussion

Self-Diffusion. Measurements were performed at overall surfactant contents of 10, 20, and 40 mmol kg^{-1}, by changing the relative amounts of the two components in the mixture. The dependence of the solute(s) self-diffusion values, D_{SDS} and D_{Bola}, on the mole fraction of the components in the mixture is reported in Figure 3. D values relative to different series, two of which are reported in Figure 3, are superimposable at intermediate mole fractions. Significant differences between the series (usually to within 5−10%) are observed at high SDS, or Bola C-16, mole fractions. This is because the fast contributions, ascribed to the molecular species, are dominant when the overall surfactant concentration is low.

The measured self-diffusion can be expressed in terms of a two-site approximation as[27]

$$D = D_{mon}cmc + D_{mic}(c_{tot} - cmc) \tag{1}$$

where $D_{mic} \ll D_{mon}$ and the cmc depends the mole ratios between SDS and Bola C-16. When knowledge of the aggregate self-diffusion, D_{mic}, is required, relatively concentrated mixtures are
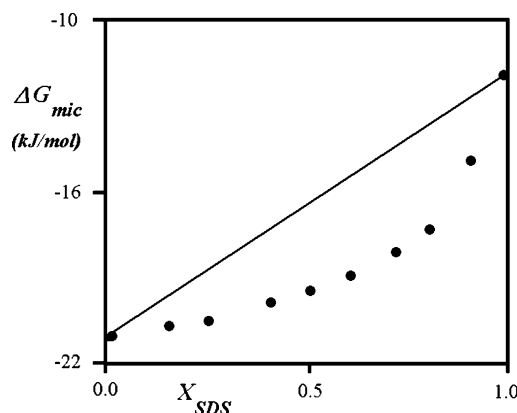

Figure 4. Gibbs energy of micelle formation, $\Delta G_{mic} = RT$ ln cmc$_{mix,mic}$ (in kJ mol^{-1}), as a function of the mole fraction of SDS in the mixture, X_{SDS}, at 25.0 °C. The full line indicates the ideality of mixing behavior.

used. The errors inherent to eq 1 are significant in pure SDS compared to the mixed systems because the former has much higher cmc values. However, D_{mic} of pure SDS is close to that reported in the literature.[28]

Compared to the mother systems, mixing of the two components results in the formation of large aggregates. In the investigated region, the average aggregate radius, R_H, increases five or six times compared to that of the mother solutions. The maximum R_H value, inferred by elaborating the data in terms of the Einstein−Stokes equation, is concomitant with the minimum D_{NMR} value in Figure 3. The optimal stoichiometry of mixed aggregates, expected from the number of crown units in Bola C-16, is not fulfilled, and trapping of Na$^+$ ions into the crown ether units is not complete under the present experimental conditions. Presumably, changes in R_H values are the result of an increase in the micelle axial ratios because of the packing of SDS and Bola C-16 units into ellipsoidal aggregates.

Self-diffusion data strongly support the formation of mixed micelles over the whole mole fraction range, and aggregates rich in one component do not occur. According to experiments, there is no significant difference in the self-diffusive behavior of the two substances in the mixed systems, and D_{NMR} values relative to SDS and Bola C-16 overlap. Thus, both components coexist in the aggregates, and no microphase separation occurs.[29]

Thermodynamics of Micelle Formation. As a result of sodium ion complexation, the mutual interactions between the polar headgroups, and alkyl chain packing, mixtures composed of Bola C-16 and SDS form mixed micelles. As indicated in Figure 4, the behavior of the mixtures is quite different from the one expected when the ideality of mixing holds. In former approaches reported so far, the validity of regular solution theory[30] is accepted, and it is assumed that "the free monomer to have an activity coefficient of unity".[31] These are oversimplifications because surfactant solutions may be nonideal even well below the cmc.[32−34] To overcome such questions, an independent model

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is developed here. The cmc (the concentration above which added surfactant preferentially enters into aggregates) is the saturation threshold for the molecular species.[35] In such a definition, the difference in composition between the molecular and the micellar form is immaterial because the cmc refers to the maximum concentration of molecular surfactant.

Accordingly, the cmc in multicomponent surfactant mixtures can be expressed as[36]

$$\text{cmc}_{\text{mix}} = \left[\frac{\prod\limits_{i=2}(\gamma_i \text{cmc}_i)}{\sum\limits_{i=2}(\gamma_i X_i \text{cmc}_i)}\right] = \left[\frac{(\gamma_2 \text{cmc}_2)(\gamma_3 \text{cmc}_3)}{(\gamma_2 X_2 \text{cmc}_2) + (\gamma_3 X_3 \text{cmc}_3)}\right] \quad (2)$$

where cmc_{mix} is the critical concentration of the mixture, X_i is the mole fraction of the ith component in it, γ_i is the solute activity coefficient in the micelle, and cmc_i is the saturation concentration, above which the surfactant preferentially enters into aggregates.[35,37] According to Holland and Rubingh, the monomer concentration of a component in mixed systems at the critical point is simply its mole fraction as solute times the cmc.[31]

Equation 2 applies to ideal systems, when all γ_i values are unity, and nonideal systems. In binary surfactant mixtures, it reduces to

$$\left[\frac{1}{\text{cmc}_{\text{mix}}}\right] = \left\{\left[\frac{X_2}{\gamma_3 \text{cmc}_3}\right] + \left[\frac{1 - X_2}{\gamma_2 \text{cmc}_2}\right]\right\} \quad (3)$$

where the meaning of the symbols is the same as before and the constraint $\Sigma_{i=1} X_i = 1$ holds.

In terms of a pseudo-phase-separation approach,[35] the Gibbs energy of mixed micelle formation, $\Delta G_{\text{mix,mic}}$, can be written as

$$\Delta G_{\text{mix,mic}} = RT \ln\left\{\frac{[\prod\limits_{i=2}(\gamma_i \text{cmc}_i)]}{[\sum\limits_{i=2}(\gamma_i X_i \text{cmc}_i)]}\right\} = $$

$$RT \ln\left[\frac{(\gamma_2 \text{cmc}_2)(\gamma_3 \text{cmc}_3)}{(\gamma_2 X_2 \text{cmc}_2) + (\gamma_3 X_3 \text{cmc}_3)}\right] \quad (4)$$

In ideal systems, the above relation reduces to

$$\left[\frac{\Delta G°_{\text{mix,mic}}}{RT}\right] = \ln[\prod\limits_{i=2}(\text{cmc}_i)] - \ln[\sum\limits_{i=2}(X_i \text{cmc}_i)] = $$

$$\ln(\text{cmc}_2 \text{cmc}_3) - \ln[X_2 \text{cmc}_2 + X_3 \text{cmc}_3] = $$

$$\ln(\text{cmc}_2 \text{cmc}_3) - \ln[X_2 \text{cmc}_2 + (1 - X_2)\text{cmc}_3] \quad (4')$$

which is a reference value for micelle formation. Thus, micelle formation is concomitant with nonideality effects in both molecular and micellar form. Combining eq 4′ with experimental cmc_{mix} values gives the excess Gibbs energy associated with the formation of mixed micelles, $\Delta G_{\text{exc,mix}}$, according to

$$\frac{\Delta G_{\text{exc,mix}}}{RT} = \frac{[\Delta G_{\text{mix,mic}} - \Delta G°_{\text{mix,mic}}]}{RT} = \ln\left[\frac{\prod\limits_{i=2}\gamma_i}{\sum\limits_{i=2}\gamma_i}\right] = \ln\left[\frac{\gamma_2 \gamma_3}{\gamma_2 + \gamma_3}\right] \quad (5)$$

In regular solution theory,[38–40] the following relation holds

$$\gamma_i = \exp[\beta(X_i)^2] \quad (6)$$

and

$$\left[\frac{\prod\limits_{i=2}\beta X_i^2}{\sum\limits_{i=2}\beta X_i^2}\right] = \ln[\prod\limits_{i=2}\gamma_i] - \ln[\sum\limits_{i=2}\gamma_i] = \beta\left[\frac{X_2^2 X_3^2}{X_2^2 + X_3^2}\right] \quad (7)$$

where β is the solute–solute interaction parameter in micelles ($\beta = NZ\omega/RT$).

If β does not depend on concentration,[41] then eq 7 gives

$$\beta = \Delta G_{\text{exc,mic}}\left[\frac{X_2^2 + X_3^2}{X_2^2 X_3^2}\right] \quad (8)$$

from which the solute–solute interaction parameter is obtained. The value of β is -7.6 ± 0.8 RT units. Comparison with different surfactant mixtures is satisfactory. The β value relative to the system SDS/C_8EO_6 is -4.1 RT units, that for SDS/N-dodecyl-sulfobetaine mixtures is -7.8, and the one relative to decyltrimethylammonium bromide/sodium decyl sulfate is -18.5.[30,41] Thus, the present system has β values close to those for mixtures of anionic and nonionic, or zwitterionic, species.

The procedure leading to eq 8 is different from those developed by Rubingh,[41,42] Rosen,[46] and Moroi.[30,47] (Note that eq 6 in ref 31 and eq 7 in ref 42, from which Rubingh's theory is developed, are not correct. See the Appendix.) In the present form, the thermodynamic model gives reasonable cmc results, consistent with experimentally available ones.

$\Delta G_{\text{exc,mic}}$ is reported as a function of SDS mole fraction in Figure 5. The function is nearly symmetric with respect to the mole fraction. This point needs to be considered in more detail. Keeping in mind that each Bola C-16 molecule has two groups capable of forming complexes with sodium ions, the maximum stability should be observed when the charge neutralization is complete (0.33 Bola C-16 mole fraction). This condition, perhaps, would presumably force the alkyl groups of Bola C-16 to have

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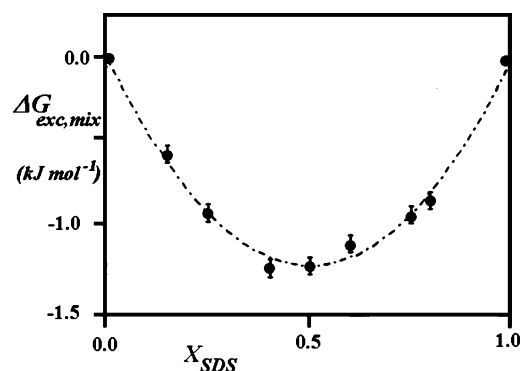(47) Moroi, Y.; Matuura, R. *J. Colloid Interface Sci.* **1988**, *125*, 456–462.

Figure 5. Plot of the excess function, $\Delta G_{exc,mic} = RT\{\ln(\gamma_2\gamma_3) - \ln(\gamma_2 + \gamma_3)\}$, as a function of the SDS mole fraction in the mixture, X_{SDS}, at 25.0 °C. The line was calculated for a β parameter of -7.6 RT units.

Table 1. Average Surface Area, A, and Excess Surface Area, A_{exc}, as a Function of the SDS Mole Fraction, X_{SDS}, at 25.0 °C and Weight Percent Values

A (Å^2)	A_{exc} (Å^2)	X_{SDS}	Bola C-16 wt %
55.5	0.00	1.000	0.000
39.1	-20.5	0.936	15.02
33.1	-30.6	0.859	30.23
38.5	-30.8	0.717	50.04
45.4	-29.3	0.516	70.35
58.2	-20.7	0.309	85.14
83.0	0.00	0.000	100.0

high-energy conformations, with dramatic consequences for the stability of mixed aggregates.

Similar thermodynamic approaches are extended to surface adsorption. Surface tension data below the cmc can be expressed according to the Gibbs relation as

$$d\pi = \sum_{i=2} \Gamma_{i,1}\, d\mu_i = -RT\sum_{i=2} \Gamma_{i,1}[(d\ln X_i) + (d\ln\gamma_i)] \tag{9}$$

where $\Gamma_{i,1}$ values are the solute excess concentrations with respect to the solvent and π is the surface pressure. Rewriting eq 9 in terms of the surface excess concentration leads to

$$\Delta G_{surf,exc} = \int_{\pi°}^{\pi} (A_{2,3} - N_2 A_2 - N_3 A_3)\, d\pi \tag{10}$$

where A_2 and A_3 are the molecular areas of the pure components, $A_{2,3}$ is the area occupied by the ideal mixed film upon compression, and π is the surface pressure required to compress (or expand) the system to its equilibrium conditions. The latter quantity is related to the surface excess of the components in mixed systems (when interactions between surfactants occur).[43,47] An elaboration of eqs 9 and 10 gives relations similar to those developed in the bulk and can be developed to get the surface interaction parameter, β_s. The behavior reported in Table 1 reflects the effects due to the different molecular areas of Bola C-16 and SDS and is ascribed to the interactions between them, which are modulated by the nonideality of mixing terms.[48]

SANS. The intensities obtained for the Bola C-16/SDS/D$_2$O system at 4.00 wt % surfactant are reported in Figure 6. The curve shape and the peak position unequivocally confirm the occurrence of globular aggregates. The scattered intensity for the mixed systems increases with SDS mole fraction, X_{SDS}, reaches a maximum at 0.72, and decreases thereafter. At the same time, the peak position moves toward higher Q values. The intensities obtained for the same system at 0.80 overall surfactant wt % are reported in Figure 7. The same considerations also apply to such data.
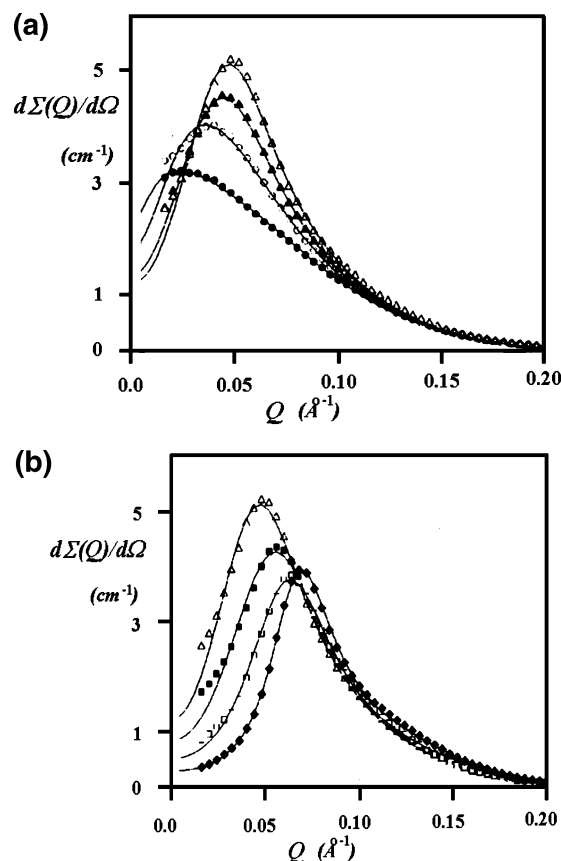

(a)

(b)

Figure 6. (a) SANS differential cross section, $d\Sigma(Q)/d\Omega$ (cm^{-1}), as a function of the momentum transfer, Q (Å^{-1}), for the Bola C-16/SDS/D$_2$O system at 25.0 °C. The overall surfactant content is 0.80 wt. The SDS mole fractions are 0.0 (●), 0.27 (○), 0.46 (▲), and 0.72 (△). (b) Same plot for mole fractions of 0.72 (△), 0.81 (■), 0.89 (□), and 1.0 (◆), respectively. The calculated intensities are reported as lines.

The SANS differential cross section for the micellar aggregates can be calculated from[49]

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right) = N_p P(Q)\, S(Q) - N_p \Delta(Q) + C \tag{11}$$

where N_P is the particle number density, $P(Q) = \langle F(Q)\rangle^2$, $F(Q)$ is the scattering due to a single particle,[50] and $S(Q)$ is the structure function related to interparticle interactions. $\Delta(Q) = \langle F(Q)\rangle^2 - \langle F(Q)^2\rangle$ is zero for spherical particles and nonzero when deviations from spherical symmetry or from a monodisperse distribution of spheres occur. The C term in eq 11 accounts for the incoherent scattering and the instrumental background.

SANS curves can be fitted by means of eq 11, provided some quantities of physical interest and realistic models for $P(Q)$ and $S(Q)$ functions are introduced. $P(Q)$ depends on micelle size and shape and on the scattering length densities of the various regions in the micellar aggregates such as the aggregate core and shell, ρ_1 and ρ_2, respectively, as well as on the solvent scattering length density, ρ_S. $S(Q)$ is related to the volume fraction of the dispersed phase, Φ, and to the size of the aggregates and is proportional to their net charge, Z. In the fitting procedure, each contribution

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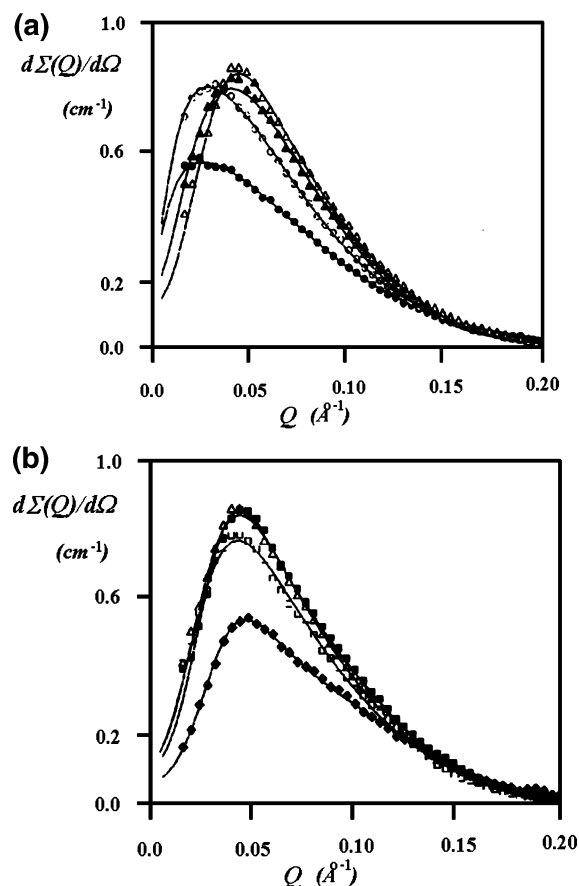
(a)

(b)

Figure 7. (a) SANS differential cross section, $d\Sigma(Q)/d\Omega$ (cm^{-1}), as a function of Q (Å^{-1}) for the Bola C-16/SDS/D$_2$O system at 25.0 °C. The overall surfactant content is 4.00 wt. The SDS mole fractions are 0.0 (●), 0.27 (○), 0.46 (▲), and 0.72 (△). (b) Same plot for mole fractions of 0.72 (△), 0.81 (■), 0.89 (□), and 1.0 (♦), respectively. The intensities calculated by the model are reported as lines.

Table 2. Group Parameters Used in Modeling Experimental SANS Data

	$10^{12}\Sigma b_i$ (cm)^a	V (Å^3)	$10^{-10} \rho$ (cm^{-2})^b	hyd. no.
Bola C-16		1172		
N-aza-18-crown-6	2.844	370.8	0.767	
Na$^+$	0.363	3.94	9.21	6
H$^+$	−0.374			
−CH$_3$	−0.457	54.3	−0.842	
−CH$_2$	−0.083	26.9	−0.308	
−SO$_4^-$	2.607	57.9	4.50	4
D$_2$O	1.91	30.2	6.34	

^{a} b_i = scattering length[56]; V = group volume.[57,58] ^{b} ρ = scattering length density; hyd. no. = hydration number.[59]

to the overall intensity was weighted by the reciprocal of variance. To reduce the number of fitting parameters, C terms in eq 11 were evaluated from the slope of the linear regression of $Q^4I(Q)$ versus Q^4 in the Porod region of the scattering curve.[51]

$S(Q)$ was calculated by the rescaled mean spherical approximation[52,53] (RMSA), assuming the interaction potential to be the sum of hard-sphere and Coulombic contributions for both Bola C-16 and SDS. Details of the computational procedures are given elsewhere.[54]

Binary Systems. In the computation of the form factor for SDS micelles, a previously described model is used.[54] Micelles are considered to be prolate ellipsoids whose core contains the alkyl chains; the shell consists of the headgroups, bound counterions, and water of hydration. The minor semiaxis of the micelle core is fixed to the length of the fully extended C_{12} alkyl chain (16.68 Å).[55] The core axial ratio, ϵ_c, is determined from the computed volume of the aggregates. A uniform shell thickness, indicated as "thick" in the following text, is assumed. This assumption implies that ϵ_c may differ from the micelle axial ratio, ϵ_m. Only two adjustable parameters are used in the fitting procedure: Z and the aggregation number, ν. thick is derived from the shell volume once Z and ν are known.

A model reported in previous work[10,52] is used in the computation of the form factor for Bola C-16 micelles. It is the result of an optimization procedure accounting for the possible molecular conformations of Bola C-16. The bond between the nitrogen atom in the crown ether and the first carbon in the hexadecyl chain forms an angle of about 119° with respect to the plane defined by the crown ether moiety. Accordingly, part of the alkyl chain can be located in the shell. According to numerical calculations on the distribution of CH$_2$ groups between the core and the shell, the best agreement with experimental data is obtained when the core contains 14 methylene units. The shell contains two CH$_2$ groups, the cryptand moieties per molecule, and the number of water molecules, bound and free, required to fill the shell volume. Micelles are assumed to be prolate ellipsoids. Z, ν, and ϵ_c were used as adjustable parameters in the fitting procedure. To determine the shell volume, its thickness, thick, is used as an additional adjustable parameter. The number of bound and free water molecules was computed from the shell volume. The scattering length densities of the various groups, computed from the atomic scattering ones[56] and from the values reported in the literature,[57,58] are summarized in Table 2 for all systems.

The calculated intensities for both binary systems, obtained according to the above procedures, are in good agreement with experimental data. The fitting parameters, along with some derived quantities for the two concentrations examined, are reported in Table 3.

Mixed Systems. As indicated in the thermodynamic section, the free energy of mixing is negative because of strong attractive interactions between the components. The formation of mixed micelles occurs over the whole range of composition. A model describing the mixed aggregates was built up. Accordingly, the system consists of prolate ellipsoidal micelles having a hydrophobic core surrounded by a hydrophilic shell. The core contains 14 methylene groups per Bola C-16 molecule, 1 methyl, and 11 methylene groups per SDS unit. The shell has two methylenes, two cryptands (for Bola C-16), the sulfate groups and sodium ions (for SDS), whose number is determined by Z. The ratio between the two components in micelles is equivalent to the stoichiometric one.

SANS data analysis was performed by using ϵ_c, ν, Z, and thick as floating parameters. The number of water molecules per monomer, n_{H_2O}, was computed from the shell volume once the volume occupied by the components was known. For the system at high surfactant content, the computed intensities are in very

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Table 3. Parameters Derived from the Fitting Procedure for the Bola C-16/D$_2$O and SDS/D$_2$O Systems[a]

[Bola C-16] wt %	ν_T	ν_{SDS}	ν_{Bola}	$10^3 V_T$ (Å³)	ϵ_c	A_c (Å)	B_c (Å)	thick (Å)	ϵ_m	Z (u.e.)	n_{H_2O} molec	$10^2\Phi$	σ
0.80	19.7(1)		19.7	43.3	3.3(1)	8.5	28.1	9.6	2.0	1.0(1)	48.0	1.80	1.0
4.00	37.9(4)		37.9	77.9	6.6(1)	8.0	52.8	10.2	3.6	1.3(1)	32.7	7.33	1.7
[SDS]													
0.80	69.0(3)	69.0		48.5	1.2	16.7	20.0	4.5	1.2	9.4(2)	9.2	1.00	0.9
4.00	91.3(3)	91.3		60.7	1.6	16.7	28.2	4.7	1.5	20.9(3)	8.6	5.90	1.9

[a] The errors in parentheses refer to the last digit of the floating parameters. ν_T, overall aggregation numbers; ν_{SDS}, SDS aggregation numbers; ν_{Bola}, Bola C16 aggregation numbers; V_T, micelle volume; ϵ_c, core axial ratios; A_c, core minor semiaxis; B_c, core major semiaxis; thick, shell thickness; ϵ_m, micelle axial ratios; Z, micelle charge; n_{H_2O}, mean number of water molecules per headgroup; Φ, volume fraction of the dispersed phase; σ is $[\Sigma_{i=1 \to NPT} \{[(obsd_i - calcd_i)^2/n_i]/(N_{PT} - N_{PAR} + 1)\}]^{1/2}$ where the terms obsd and calcd refer to the experimental and computed intensities, respectively. N_{PT} and N_{PAR} are the number of observations and the number of parameters changed in the fitting procedure, respectively.

Table 4. Floating and Derived Parameters from the Fitting Procedure Described in the Text for the Bola C-16/SDS/D$_2$O System at 25 °C[a]

χ_{SDS}	ν_T	ν_{SDS}	ν_{Bola}	$10^3 V_T$ (Å³)	ϵ_c	A_c (Å)	B_c (Å)	thick (Å)	ϵ_m	Z (u.e.)	n_{H_2O} moles	$10^2\Phi$	σ
					0.80 wt %								
0.0	37.7(4)		37.7	77.9	5.9(1)	8.3	48.9	9.5	3.3	1.0(1)	30.0	7.30	1.7
0.125	67.2(9)	18.1	49.1	113.1	6.4(1)	9.7	62.1	9.7	3.7	3.5(1)	24.5	7.25	1.9
0.250	91.3(9)	42.0	49.3	131.8	5.7(1)	11.1	63.3	9.5	3.6	6.4(2)	20.6	7.16	2.2
0.500	128.8(4)	92.7	36.1	138.8	4.5(1)	13.4	60.3	8.4	3.2	7.9(1)	15.3	6.89	3.2
0.625	107(1)	86.7	20.3	101.1	3.3(1)	14.0	46.2	7.3	2.5	8.6(2)	13.4	6.73	3.8
0.750	94.5(8)	84.1	10.4	80.5	2.7(1)	14.3	38.6	6.3	2.2	11.8(3)	11.5	6.43	3.8
1.0	91.5(3)	91.5		60.7	1.7(1)	16.6	28.2	4.7	1.5	20.9(3)	8.6	5.90	1.9
					4.00 wt %								
0.0	20.9(1)		20.9	43.3	3.7(1)	8.0	29.6	8.5	2.3	1.3(1)	30.0	1.45	1.0
0.125	36.6(2)	9.9	26.7	63.2	3.0(1)	10.2	30.6	9.1	2.1	2.0(1)	24.5	1.43	1.0
0.250	44.9(3)	20.6	24.3	62.9	2.1(1)	12.3	25.8	8.8	1.6	4.6(2)	20.5	1.41	1.8
0.500	61.7(2)	44.4	17.3	67.7	1.6(1)	15.0	24.0	7.6	1.4	7.2(2)	15.1	1.31	1.2
0.625	66.9(4)	54.2	12.7	62.9	1.9(1)	14.3	27.2	6.8	1.6	6.5(2)	13.3	1.26	1.7
0.750	78.9(4)	70.2	8.7	66.2	1(2)	18.7	18.7	6.4	1.0	8.7(3)	11.6	1.23	1.7
1.0	69.0(3)	69.0		48.5	1.2(1)	16.7	20.0	4.6	1.2	9.4(2)	9.2	1.00	0.9

[a] The errors refer to the last digit of the floating parameters. χ_{SDS}, SDS mole fraction; other terms are the same as in Table 3.

good agreement with the experimental ones. At low surfactant concentrations, conversely, the fit quality is rather poor. This is a consequence of the aggregate size and of the diffuse core–shell and shell–solvent interfaces that do not allow the evaluation of the shell thickness and, hence, n_{H_2O}. In concentrated solutions, such values are close to those of the Bola C-16/water system.[10] Thus, it was assumed that they are constant at all concentrations and equal to the values expected from stoichiometry. This allows the calculation of thick values and reduces the number of floating parameters.

The volume of the aggregates was calculated from ν and from the molar volumes of the components. N_p was derived from ν and from the stoichiometric concentration, corrected for the cmc. Results relative to the above procedure are reported in Figures 6 and 7. As can be seen, the agreement between experimental scattering intensities and computed ones is fairly good. Values of the floating parameters and some derived quantities are summarized in Table 4. The data analysis of the binary systems was repeated using the latter model and compared with previous findings. The results (Table 4) are still in good agreement with those formerly discussed.

To strengthen the model, the data fitting was repeated by introducing as an additional parameter a floating intensity multiplying factor, A. Such a value is a correction for the absolute intensity calibration. The structural parameters computed by the above procedure, reported in Table 5, are equivalent, within the limit of experimental accuracy, to those formerly reported. Because A values in Table 5 randomly vary from system to system, the confidence in the model is strengthened. The aggregation numbers and micelle volumes are reported in Figure 8 as a function of X_{SDS}. They change and reach a maximum whose intensity and position depend on the overall surfactant content.

Mixtures of nonionic and anionic surfactants have been investigated from a structural viewpoint.[60–63] The one most similar to the present system deals with [SDS/C$_{12}$E$_6$] mixtures. In such a system, the aggregation numbers monotonically increase with the mole fraction of C$_{12}$E$_6$.[62] Notwithstanding the similarity of C$_{12}$E$_6$ with Bola C-16 (the headgroups of both surfactants contain ethoxylated groups), the complexing ability of Bola C-16 is presumably responsible for the nonideality of mixing. This effect is concomitant with the occurrence of a maximum in aggregation numbers. A strong increase in micelle size, characterized by the presence of a maximum, has been observed for mixtures of anionic and cationic surfactants.[63] These findings confirm that the present system is to be considered as a very peculiar mixture of cationic and anionic surfactants. The strength of electrostatic interactions, reflected in the excess free energy of mixing, is responsible for the observed trends in aggregation numbers. It could be responsible for the behavior observed in aggregation numbers of concentrated systems. At low surfactant content, the headgroups are quite distant from each other; when the concentration increases, the reciprocal attraction between them accounts for the strong deviations from the behavior observed at low concentrations. Higher concentrations imply more charged aza-crown groups because of the constraints dictated by the complexation equilibrium.

In mixed systems, the micelle axial ratios regularly vary with composition. Slight departures from the above behavior can be

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Table 5. Floating and Derived Parameters from the Fitting Procedure Described in the Text for the Bola C-16/SDS/D₂O System at 25 °C[a]

χ_{SDS} wt	A	ν_T	ν_{SDS}	ν_{Bola}	$10^3 V_T$ (Å³)	ϵ_c	A_c (Å)	B_c (Å)	thick (Å)	ϵ_m	Z (u.e.)	n_{H_2O} moles	$10^2\Phi$	σ
							0.80 wt %							
0.0	1.04(1)	37.6(3)		37.6	78.1	6.5(1)	8.0	52.0	9.3	3.6	1.3(3)	30.0	7.30	1.1
0.125	1.02(1)	67.3(9)	18.2	49.1	113.8	6.9(2)	9.5	65.6	9.6	3.9	3.7(1)	24.5	7.25	1.7
0.250	1.04(1)	92.9(9)	42.7	50.2	132.7	6.4(2)	10.8	69.1	9.3	3.9	6.8(2)	20.6	7.16	1.8
0.500	1.03(1)	129(1)	92.9	36.1	139.6	4.9(2)	13.1	64.2	8.3	3.4	8.2(2)	15.3	6.89	2.9
0.625	0.98(1)	107(1)	86.7	20.3	101.3	3.2(1)	14.2	45.4	7.4	2.4	8.5(2)	13.4	6.73	3.8
0.750	1.01(1)	92.3(7)	82.1	10.2	78.1	2.1(1)	15.4	32.3	6.4	1.8	11.7(2)	11.5	5.90	3.0
1.0	0.99(1)	91.6(3)	91.6		60.7	1.6(1)	16.7	26.7	4.8	1.5	20.9(3)	8.6	5.89	1.9
							4.00 wt %							
0.0	0.93(1)	22.1(2)		22.1	44.9	3.1(1)	8.6	26.7	8.9	2.0	1.1(1)	30.0	1.45	0.8
0.125	1.10(1)	34.4(3)	9.3	25.1	59.4	3.0(1)	10.1	30.3	8.8	2.1	4.6(1)	24.4	1.43	1.1
0.250	0.98(1)	44.3(1)	20.4	23.9	64.2	3.1(1)	10.8	33.5	8.3	2.2	2.1(1)	20.7	1.41	0.9
0.500	1.02(1)	60.7(5)	43.8	16.9	66.9	1.7(1)	14.5	24.7	7.5	1.5	7.1(2)	15.1	1.31	1.2
0.625	1.10(1)	63.8(6)	51.7	12.1	62.0	1.4(1)	15.6	21.8	6.9	1.3	8.2(1)	13.2	1.25	1.0
0.750	0.96(1)	81.8(8)	72.8	9.0	71.6	1.4(1)	17.1	23.9	6.5	1.3	7.4(2)	11.7	1.16	1.2
1.0	0.99(2)	69.4(9)	69.4		47.1	1.2(1)	17.1	20.5	4.6	1.1	9.5(3)	9.2	1.00	0.9

[a] The error in parentheses refers to the last digit of the floating parameters. A, intensity multiplying factor; other terms are the same as in Tables 3 and 4.
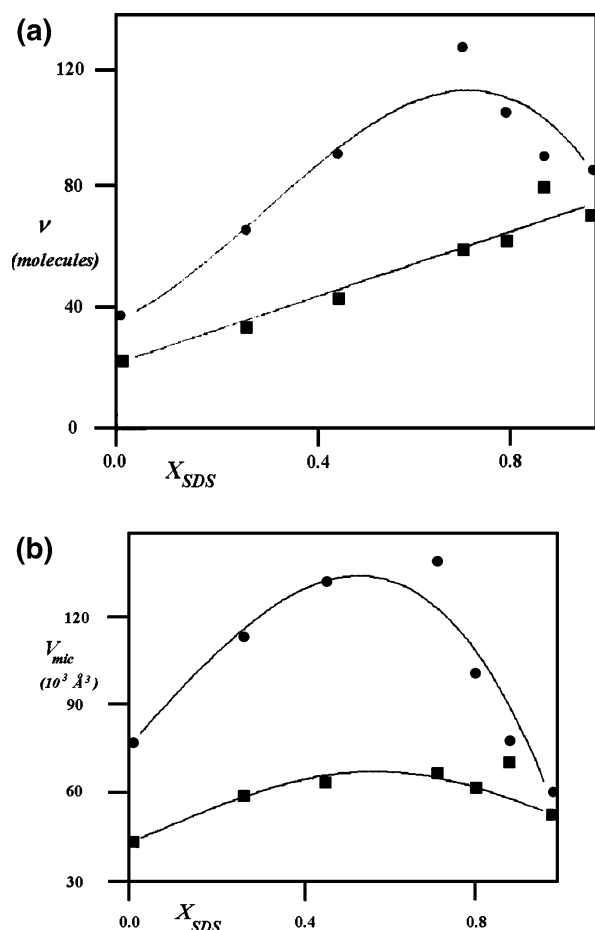

(a)

(b)

Figure 8. Aggregation numbers, ν (molecules), and micelle volume, V_{mic} (Å³) as a function of X_{SDS} in the surfactant mixture are reported in panels a and b, respectively. Total surfactant contents are 0.80 (■) and 4.00 wt (●).

observed in concentrated systems at low X_{SDS}. In Figure 9, the major and minor core semiaxes as a function of X_{SDS} for both concentrated and dilute systems are shown. The minor semiaxis length, A_c, linearly increases with SDS content, independently of the overall surfactant content, and is close to the weighted alkyl chain length value. Having let ϵ_c float, this result is not obvious. For the system at high concentration, the major semiaxis display a maximum as a function of X_{SDS}. At low concentrations, the effect is less pronounced, and the maximum value is obtained
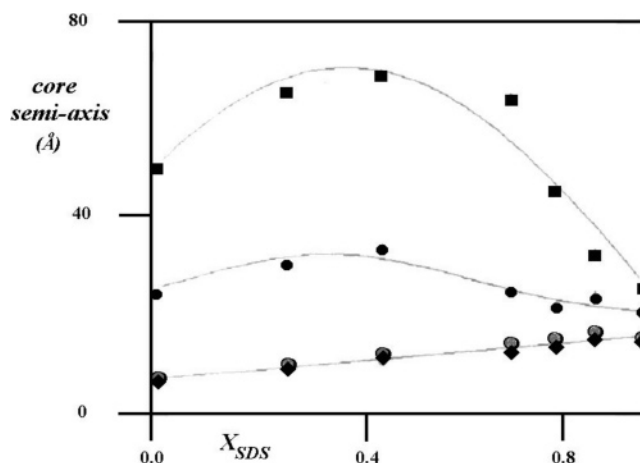

Figure 9. Core semiaxes, (Å), as a function of X_{SDS} in the surfactant mixture. Total surfactant contents are 0.80 (■) and 4.00 wt (●). Grey circles and diamonds refer to the minor core semiaxis in the same mixtures.

at lower X_{SDS}. The apparent charge increases regularly with SDS content, as expected, and the volume fraction of the dispersed phase decreases. This is a direct consequence of (i) the monotonic decrease of n_{H_2O} as a function of X_{SDS} and (ii) the choice to operate at constant total weight percent. In fact, because the density of Bola C-16 is lower than that of SDS, a reduction of the volume fraction is expected.

Conclusions

Surface tension, PFG-SE NMR, and SANS measurements were performed on aqueous solutions of Bola C-16 and SDS as a function of the overall surfactant content and by changing the mole ratios between the components. These mixtures are nonideal, as inferred from the dependence of cmc on SDS mole fraction. The interaction parameter, β, obtained from an ad hoc thermodynamic model (based on excess functions) is negative and significant. This indicates that the nonideality of mixing is essentially controlled by electrostatic interactions between SDS ions and sodium complexed by the Bola C-16 moieties. The same holds for the behavior at the air–aqueous solution interface, where a significant area reduction with respect to the ideal case is observed.

NMR self-diffusion data indicate significant growth in the size of the mixed aggregates compared to the corresponding

binary systems. The occurrence of prolate ellipsoidal micelles, inferred from SANS, supports the aforementioned hypothesis. Good agreement between experimental and calculated SANS intensities was obtained, assuming the micelle composition to be equivalent to the stoichiometric one over the whole range of composition. On increasing the SDS content, micelles grow in size along the major rotational axis.

The observed trends can be rationalized in terms of the nonideality of mixing. More significant effects and the presence of other supramolecular structures are expected to occur in strongly saline media. Peculiar effects are expected to occur in the solubilizing capacity of mixed surfactant systems and when using the above mixtures in emulsion stabilization. Applications of Bolaform-based surfactant mixtures are in biochemically oriented preparations to modulate the formation, stability, and net charge of vesicles and liposomes for controlled drug release.[64]

Appendix: Thermodynamics of Micelle Formation

We have strong doubts about the consistency of the equations developed by Rubingh[31,42] and revised later by Moroi.[30] We

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believe that the hypotheses leading to eq 7 in Rubingh's paper[42] and eq 6 in ref 31 are wrong. In fact, if

$$C_i^m = x f_i C_i$$

$$C_i^m = \alpha_i C^*$$

and

$$\sum_{i=1} x_i = 1$$

we get

$$\frac{1}{C^*} = \frac{\sum\limits_{i=1} \alpha_i}{\sum\limits_{i=1} x f_i C_i}$$

and *not*

$$\frac{1}{C^*} = \frac{\sum\limits_{i=1} \alpha_i}{\sum\limits_{i=1} f_i C_i}$$

This can also be demonstrated by rewriting the equality in different ways.

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