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# A Small-Angle Neutron Scattering (SANS) Study of Tablet-Shaped and Ribbonlike Micelles Formed from Mixtures of an Anionic and a Cationic Surfactant

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Micelles formed in mixtures of an anionic (SDS) and a cationic (DTAB) surfactant, i.e., two surfactants with identical hydrocarbon  $C_{12}$  chains, in either pure (heavy) water or 0.1 M NaBr brine at 40 °C have been investigated using small-angle neutron scattering (SANS). In contrast to common opinion, it is found that the micelles are shaped as tablets or elongated bilayer fragments, i.e., triaxial ellipsoids with half-axes  $a < b < c$ . Pure SDS as well as DTAB micelles in 0.1 M NaBr are found to be disk-shaped (oblate ellipsoids of revolution) with a half thickness  $a \approx 15$  Å and a disk radius  $b$  equal to 23–24 Å. As an oppositely charged surfactant is admixed, both SDS-rich and DTAB-rich micelles grow in size into elongated tablets with decreasing surface charge density as the overall equimolar surfactant composition is approached at a given overall surfactant concentration. The micelles also grow, because of a free monomer effect, as the mixtures are diluted at a given overall surfactant composition. In the absence of added salt, the tablet-shaped micelles grow significantly with respect to both width and length before an abrupt transition from comparatively small tablet-shaped micelles ( $a \approx 16$  Å,  $b \approx 45$  Å,  $2c \approx 300$  Å) to stacks of lamellar sheets occurs. However, when a 0.1 M NaBr solution is used as solvent, the micelles grow strongly in length but only slightly in width and, as a result, flexible ribbonlike (SDS-rich) micelles as long as several thousands of Ångströms with half-thickness  $a \approx 16$  Å and half-width  $b \approx 30$  Å are observed close to surfactant compositions where a transition to lamellar sheets is seen. An expression for the free energy of forming a tablet-shaped micelle is introduced, from which it is possible to calculate the average width and length of the micelles.

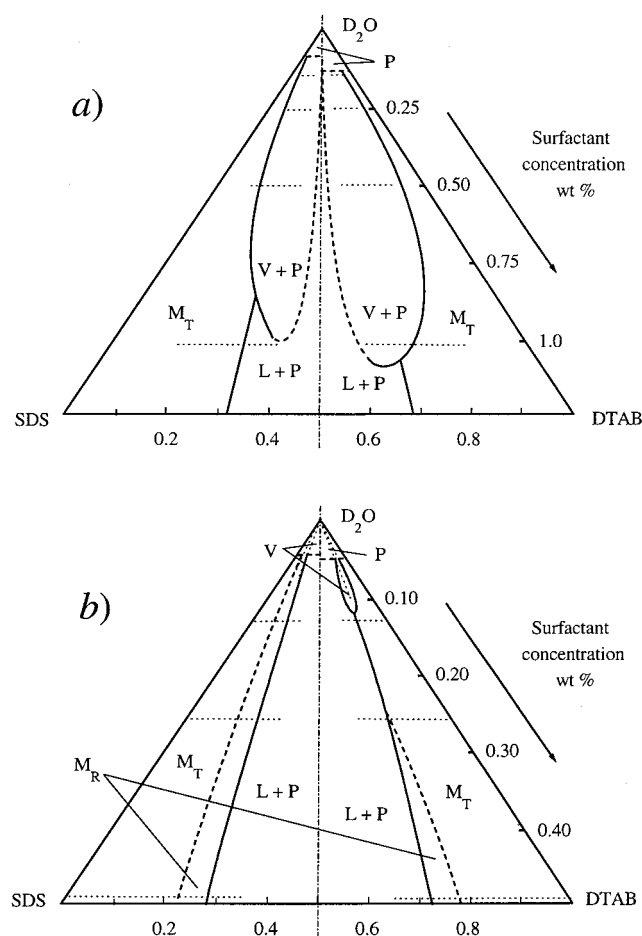
## Introduction

Above a certain concentration, ionic surfactants aggregate in order to form small droplet-like particles called micelles. The driving force for the aggregation process is the reduction of the unfavorable hydrocarbon/water contact interfacial free energy, and the largest counteracting effect is due to the unfavorable work of locating the charged headgroups, with an associated diffuse layer of counterions, at the micelle surfaces.<sup>1</sup> Because of geometrical packing constraints, the contact area between hydrocarbon and water per aggregated monomer obtains its minimum value for the noncurved geometry of a planar bilayer. However, because of the entropy of mixing counterions and solvent, the diffuse cloud of counterions surrounding each charged aggregate tends to become diluted by means of curving the interface of the aggregate. In addition, the entropy of mixing aggregates and water favors small aggregates.<sup>2</sup> As a result, ionic surfactants such as SDS (sodium dodecyl sulfate, anionic surfactant) or DTAB (dodecyltrimethylammonium bromide, cationic surfactant) form rather small, almost spherical micelles in pure water.<sup>3–5</sup> The electrostatic contribution to the free energy of forming a micelle can be influenced by means of adding a third component to the surfactant solution. The entropic gain of spreading out the counterions is substantially reduced when a conventional salt is added,<sup>6–8</sup> and the surface charge density decreases as a nonionic cosurfactant is mixed into the micelles.<sup>9–12</sup> Hence, a considerable reduction of the micelle curvature and a subsequent transition to various bilayer structures with increasing

amounts of either added salt or cosurfactant can be observed. The transition is also found theoretically from model calculations using the Poisson–Boltzmann mean field approximation in order to calculate the electrostatic free energy contribution of the surfactant aggregates without introducing any particular specific interactions between the headgroups.<sup>13</sup>

An even more dramatic change of the aggregate geometry is obtained when two oppositely charged surfactants are mixed together in an aqueous solution.<sup>14–22</sup> A variety of different equilibrated microstructures have been observed in such systems, including small globular as well as large wormlike micelles, rather small unilamellar vesicles and large lamellar sheets. A more detailed discussion of earlier studies of aqueous mixtures of SDS and DTAB has been given by us in a recent paper in which we also reported on the various microstructures found in mixtures of SDS and DTAB at 40°C in pure (heavy) water using small-angle neutron scattering (SANS) [cf. Figure 1a].<sup>22</sup> In samples with a total surfactant concentration below about 0.25–0.50 wt % we found unilamellar or oligolamellar vesicles. However, when the surfactant concentration was increased, a transition from vesicles to either micelles or stacks of lamellar sheets was observed. The data from the samples in which micelles formed were reasonably fitted with models for either cylindrical rods with swollen end caps or oblate ellipsoids of revolution. More recently, we have studied mixtures of the same surfactants, also at 40°C, using a solvent where NaBr was dissolved in  $D_2O$  at a concentration of 0.1 M [cf. Figure 1b]. The vesicles were clearly destabilized in brine, where either micelles or lamellar sheets were seen to form at the expense of the vesicles. The micelles were considerably elongated in 0.1

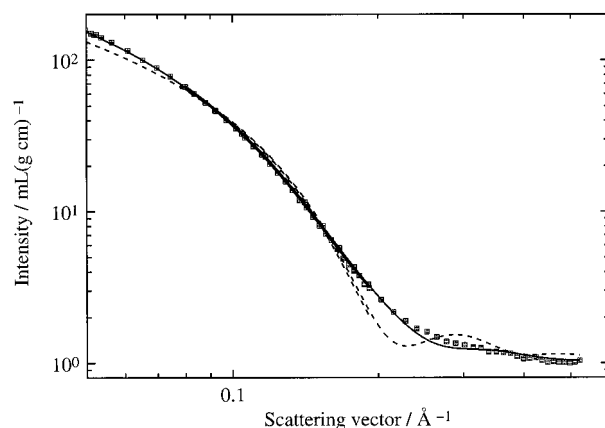
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**Figure 1.** Ternary diagrams showing the regimes of different microstructures found in mixtures of SDS and DTAB using either (a) pure  $D_2O$  or (b) 0.1 M NaBr in  $D_2O$  as solvent obtained from measurements of several samples along the dotted lines. In the former case we have found uni- or oligolamellar vesicles (V), rigid tablet-shaped micelles ( $M_T$ ), and stacks of lamellar sheets (L). In the most dilute parts and close to equimolar composition, an increasing amount of a precipitate (P) of  $DTA^+DS^-$  is formed. In the case (b) where a monovalent salt was added, some of the micelles become much elongated and the corresponding scattering data must be fitted with a model for flexible ribbonlike micelles ( $M_R$ ). There are no sharp boundaries between the regimes where micelles and vesicles are found but rather narrow domains where the two surfactant aggregates coexist.<sup>25</sup> The dashed lines between [SDS]:[DTAB] = 40:60 and 60:40 in diagram (a) were extrapolated in a similar way, done by Kaler et al. [cf. ref 14], as we have not measured any samples in this regime. Note the different scales for the axes denoting the surfactant concentration in the two diagrams.

M NaBr, and we could only fit the corresponding data assuming the rodlike micelles to have a noncircular cross-section [cf. Figure 2 and further below].<sup>23</sup> Our results for the geometry of the rather elongated aggregates have caused us to conclude that also the smaller micelles we have found are shaped as tablets with a distinct thickness, width, and length, respectively. In fact, the agreement between model fits and data for the micelles formed in the absence of added salt was substantially improved using a model for tablet-shaped (triaxial ellipsoidal) particles rather than cylindrical rods with swollen end caps or oblate disks, as was done in ref 22.

A brief outline of our results for the geometrical structure of mixed SDS/DTAB micelles has been given in a recent letter.<sup>23</sup> Below we present the details of our study as well as quantitative results for the formation of rigid tablet-shaped micelles and their growth, in either pure  $D_2O$  or in 0.1 M NaBr, with decreasing



**Figure 2.** Normalized scattering intensity as a function of the scattering vector  $q$  in the high  $q$  range for [SDS]:[DTAB] = 80:20 and [SDS] + [DTAB] = 1.0 wt %. Individual symbols represent data obtained with different combinations of neutron wavelength and sample-detector distance, and the lines correspond to the intensity smeared by the instrumental resolution. The solid lines represent the best available fit ( $0.05 < q/\text{\AA}^{-1} < 0.6$ ) assuming an elliptical cross-section, resulting in half-axes  $a = 13.4 \text{ \AA}$  and  $b = 26.7 \text{ \AA}$ . The dashed lines represent the best available fit assuming a circular cross-section, giving a cylinder radius of  $17.6 \text{ \AA}$ . The agreement of the former fit as measured by<sup>30</sup>  $\chi^2$  equals 7.5 and of the latter  $\chi^2 = 207$ .

surface charge density and, in the latter case, the subsequent formation of very long flexible ribbonlike micelles.

## Materials and Methods

**Materials.** Sodium dodecyl sulfate (SDS, 99%) was obtained from Merck, dodecyl trimethylammonium bromide (DTAB, 99%), and sodium bromide (NaBr, 99%) from Aldrich Chemical Co. and used without further purification.  $D_2O$  with 99.9 atom % D came from Aldrich Chemical Co.

**Sample Preparation.** Stock solutions containing SDS and DTAB in pure  $D_2O$  with a SDS-to-DTAB ratio ranging from 3:17 to 2:3 and from 3:2 to 17:3 were prepared by simply mixing the two surfactants with  $D_2O$  to yield an overall surfactant concentration ([SDS] + [DTAB]) of 1.0 or 5.0 wt %. The brine was prepared by mixing NaBr in  $D_2O$  to a concentration of 0.1 M. Then SDS and DTAB with proportions ranging from 0:1 to 7:13 and from 13:7 to 1:0 were mixed in the brine to yield [SDS] + [DTAB] = 1.0 wt %.  $D_2O$  was chosen in order to minimize the incoherent background from hydrogen and obtain a high scattering contrast. The final samples were then obtained by means of diluting the stock solutions to various surfactant concentrations. Each sample was equilibrated at least 20 h at  $40^\circ\text{C}$ , except the samples measured at the Institut Laue-Langevin in Grenoble, France (see further below), which were equilibrated for 5–10 h. The temperature was chosen to be sufficiently high for precipitate of  $DTA^+SDS^-$  to be dissolved at the used SDS-to-DTAB molar ratios. Micelles were found at surfactant compositions and concentrations as indicated in Tables 1 and 2.

**Methods.** The small-angle neutron scattering (SANS) experiments were performed at the SANS instrument at the DR3 reactor at Risø National Laboratory, Denmark.<sup>24</sup> A range of scattering vectors  $q$  from 0.004 to  $0.5 \text{ \AA}^{-1}$  was covered by four combinations of neutron wavelength (3 and  $10 \text{ \AA}$ ) and sample-to-detector distances (1–6 m). The wavelength resolution was 18% (full width at half-maximum value). Some of the samples ([SDS]:[DTAB] = 15:85 and 20:80 at 0.25 and 0.5 wt % and 80:20 and 85:15 at 0.125 and 0.25 wt % in brine) were measured at the D22 SANS instrument at Institut Laue-Langevin

**TABLE 1: Results from SANS Data Analyses of Samples Where Mixed SDS/DTAB Micelles form at 40 °C in D<sub>2</sub>O in the Absence of Added Salt<sup>a</sup>**

[SDS]:[DTAB]	0.50 wt %	1.0 wt %	2.5 wt %	5.0 wt %
15:85	vesicles & micelles	$a = 16.0$ $b = 27.7$ $c = 37.7$ $z_{\text{eff}}/z_{\text{id}} = 0.12$	not measured	not measured
20:80	vesicles	$a = 17.6$ $b = 31.9$ $c = 55.5$ $z_{\text{eff}}/z_{\text{id}} = 0.13$	$a = 16.9$ $b = 30.2$ $c = 43.7$ $z_{\text{eff}}/z_{\text{id}} = 0.48$	$a = 17.3$ $b = 28.4$ $c = 44.9$ $z_{\text{eff}}/z_{\text{id}} = 0.22$
25:75	vesicles	$a = 16.8$ $b = 39.3$ $c = 122$ $z_{\text{eff}}/z_{\text{id}} = 0.08$	not measured	not measured
30:70	vesicles	vesicles	$a = 17.9$ $b = 37.0$ $c = 111$ $z_{\text{eff}}/z_{\text{id}} = 0.04$	$a = 18.1$ $b = 32.8$ $c = 138$ $z_{\text{eff}}/z_{\text{id}} = 0.13$
70:30	vesicles	$\xi = 13.6$ $b = 47.0$ $c = 136$ $z_{\text{eff}}/z_{\text{id}} = 0.18$	$a = 16.7$ $b = 41.2$ $c = 163$ $z_{\text{eff}}/z_{\text{id}} = 0.48$	$a = 16.6$ $b = 41.5$ $c = 160$ $z_{\text{eff}}/z_{\text{id}} = 0.26$
75:25	vesicles & micelles	$a = 15.7$ $b = 34.9$ $c = 61.3$ $z_{\text{eff}}/z_{\text{id}} = 0.25$	not measured	not measured
80:20	$a = 15.7$ $b = 32.4$ $c = 46.6$ $z_{\text{eff}}/z_{\text{id}} = 0.13$	$a = 16.2$ $b = 29.9$ $c = 42.7$ $z_{\text{eff}}/z_{\text{id}} = 0.20$	$a = 16.0$ $b = 29.8$ $c = 45.5$ $z_{\text{eff}}/z_{\text{id}} = 0.31$	$a = 16.1$ $b = 28.5$ $c = 52.1$ $z_{\text{eff}}/z_{\text{id}} = 0.33$
85:15	$a = 15.8$ $b = 22.7$ $c = 45.2$ $z_{\text{eff}}/z_{\text{id}} = 0.11$	$a = 15.0$ $b = 25.7$ $c = 33.0$ $z_{\text{eff}}/z_{\text{id}} = 0.21$	not measured	not measured

<sup>a</sup> The data were fitted with a model for monodisperse triaxial ellipsoids with half-axes  $a$  (related to the thickness)  $< b$  (related to the width)  $< c$  (related to the length). The data of the sample for which [SDS]:[DTAB] = 70:30 and [SDS] + [DTAB] = 1.0 wt % were best fitted with a model for a flat elliptical disk with half-thickness  $\xi$  and half-axes  $b$  and  $c$ . All spatial dimensions are given in angstroms (Å) and typical values of the errors of  $a$  and  $b$  are  $\pm 0.2$  and  $\pm 0.5$  Å, respectively. A structure factor had to be included in our analyses to account for the comparatively large double-layer interactions between macroions with an effective charge  $z_{\text{eff}}$ . The ideal charge  $z_{\text{id}}$  is the charge of a micelle for which the counterions are fully dissociated.

(ILL), Grenoble, France, in connection with a SANS study of vesicles formed in mixtures of SDS and DTAB.<sup>25</sup> The range of scattering vectors between 0.0015 and 0.4 Å<sup>-1</sup> was covered by three combinations of neutron wavelengths (8 and 12 Å) and sample-to-detector distances (1.4–18 m) and the wavelength resolution was 10%. The samples 85:15 at 0.125 and 0.25 wt % were only measured at the ILL and not at Risø.

The samples were kept in quartz cells (Hellma) with a path length of either 2 or 5 mm depending on concentration. The raw spectra were corrected for background from the solvent, sample cell, and other sources by conventional procedures.<sup>26</sup> The two-dimensional isotropic scattering spectra were azimuthally averaged, converted to an absolute scale and corrected for detector efficiency by dividing by the incoherent scattering spectra of pure water measured in a 1 mm cell.<sup>27</sup> The scattering intensity was furthermore normalized by dividing with the concentrations of solute (SDS and DTAB).

The average excess scattering length density per unit mass of the solute  $\Delta\rho_m$  was calculated from the known SDS-to-DTAB molar ratio using the appropriate molecular volumes and molecular weights of the monomers.<sup>28</sup>

Throughout, the data analysis corrections were made for instrumental smearing.<sup>24,29</sup> For each instrumental setting the ideal model scattering curves were smeared by the appropriate resolution function when the model scattering intensity was compared with the measured one by means of least-squares methods. The parameters in the model were optimized by means

of conventional least-squares analysis and the errors of the parameters were calculated by conventional methods.<sup>30,31</sup>

## Data Analyses and Results

**Analyses.** Indirect Fourier transformation (IFT) can provide useful information of the structure and dimensions of surfactant aggregates.<sup>32,33</sup> By this method the pair distance distribution function (PDDF) is determined. It is equal to the self-correlation function of the excess scattering length density multiplied by the distance squared. The PDDF for the comparatively small micelles formed in the absence of added salt was obtained by means of performing indirect Fourier transformations of the corresponding scattering data [not shown]. Since the PDDF vanishes at a much higher value than the length of a fully extended surfactant molecule, it is evident that the micelles are rather anisotropic. In 0.1 M NaBr the micelles in some of the samples appear to be larger and they show the typical  $q^{-1}$  behavior for rodlike particles. The cross-section pair distance distribution function  $p_{\text{cs}}(R)$  for one of these samples is given in Figure 3, from which it is seen that the maximum cross-section distance ( $\sim 55$  Å) is much larger than twice a fully extended surfactant molecule ( $= 2 \times 16.7$  Å plus contribution from the headgroups). The tail-like behavior of the function at large  $R$ -values is typical of that for an elliptical cross-section.<sup>34</sup> The corresponding radial cross-section scattering length density profile  $\Delta\rho(R)$  [not shown], which is obtained from  $p_{\text{cs}}(R)$  using the square-root deconvolution procedure,<sup>35,36</sup> does not appear

**TABLE 2: Results from SANS Data Analyses of Samples Where Mixed SDS/DTAB Micelles Form at 40 °C in a 0.1 M NaBr D<sub>2</sub>O Solution<sup>a</sup>**

[SDS]:[DTAB]	0.125 wt %	0.25 wt %	0.50 wt %	1.0 wt %
0:100	not measured	not measured	$a = 15.0$ $b = c = 23.9$ $z_{\text{eff}}/z_{\text{id}} = 0.50$	$a = 15.0$ $b = c = 24.0$ $z_{\text{eff}}/z_{\text{id}} = 0.27$
5:95	not measured	not measured	$a = 15.7$ $b = 25.6$ $c = 26.2$ $z_{\text{eff}}/z_{\text{id}} = 0.42$	$a = 15.9$ $b = 25.3$ $c = 26.3$ $z_{\text{eff}}/z_{\text{id}} = 0.29$
10:90	$a = 14.7$ $b = 29.8$ $c = 100$	$a = 15.2$ $b = 25.7$ $c = 38.6$	$a = 15.7$ $b = 24.7$ $c = 34.6$ $z_{\text{eff}}/z_{\text{id}} = 1.0$	$a = 15.3$ $b = 25.6$ $c = 31.0$ $z_{\text{eff}}/z_{\text{id}} = 0.72$
15:85	vesicles	$a = 15.4$ $b = 29.4$ $\langle L \rangle = 98.0$ $\sigma_L/\langle L \rangle = 0.80$	$a = 15.7$ $b = 26.0$ $c = 48.0$	$a = 15.8$ $b = 26.1$ $c = 43.5$
20:80	vesicles	$a = 14.4$ $b = 32.8$ $\langle L \rangle = 392$ $\sigma_L/\langle L \rangle = 0.18$	$a = 14.6$ $b = 28.6$ $\langle L \rangle = 199$ $\sigma_L/\langle L \rangle \approx 1$	$a = 14.7$ $b = 27.6$ $\langle L \rangle = 139$ $\sigma_L/\langle L \rangle \approx 1$
25:75	lamellae	lamellae	$a = 14.4$ $b = 31.5$ $\langle L \rangle = 924$ $\sigma_L/\langle L \rangle = 0.59$ $l_p = 136$ lamellae	$a = 14.7$ $b = 28.5$ $L = 479$ $\sigma_L/\langle L \rangle = 0$
30:70	lamellae	lamellae	lamellae	$a = 14.3$ $b = 31.5$ $\langle L \rangle = 3100$ $\sigma_L/\langle L \rangle \approx 1$ $l_p = 62$
75:25	lamellae	$a = 13.2$ $b = 32.1$ $l_p = 99$	$a = 13.5$ $b = 30.4$ $l_p = 171$	$a = 13.7$ $b = 29.5$ $l_p = 222$
80:20	$a = 13.7$ $b = 30.2$ $\langle L \rangle = 916$ $\sigma_L/\langle L \rangle = 0.46$ $l_p = 208$	$a = 13.4$ $b = 27.5$ $\langle L \rangle = 472$ $\sigma_L/\langle L \rangle = 0.60$	$a = 13.6$ $b = 27.2$ $\langle L \rangle = 439$ $\sigma_L/\langle L \rangle \approx 1$	$a = 13.5$ $b = 26.7$ $\langle L \rangle = 327$ $\sigma_L/\langle L \rangle \approx 1$
85:15	$a = 14.2$ $b = 27.6$ $\langle L \rangle = 129$ $\sigma_L/\langle L \rangle = 0.79$	$a = 14.3$ $b = 27.1$ $\langle L \rangle = 72.4$ $\sigma_L/\langle L \rangle = 0.77$	$a = 14.9$ $b = 25.7$ $c = 56.0$	$a = 14.7$ $b = 25.6$ $c = 54.3$
90:10	$a = 15.4$ $b = 24.1$ $c = 41.1$	$a = 14.8$ $b = 24.0$ $c = 37.3$	$a = 14.1$ $b = 24.2$ $c = 35.5$ $z_{\text{eff}}/z_{\text{id}} = 1.1$	$a = 14.1$ $b = 25.4$ $c = 33.2$ $z_{\text{eff}}/z_{\text{id}} = 0.99$
95:5	not measured	not measured	$a = 15.1$ $b = 25.3$ $c = 26.3$ $z_{\text{eff}}/z_{\text{id}} = 0.36$	$a = 15.0$ $b = 24.9$ $c = 26.7$ $z_{\text{eff}}/z_{\text{id}} = 0.41$
100:0	not measured	not measured	$a = 14.6$ $b = c = 23.3$ $z_{\text{eff}}/z_{\text{id}} = 0.37$	$a = 14.7$ $b = c = 23.2$ $z_{\text{eff}}/z_{\text{id}} = 0.60$

<sup>a</sup> The data were fitted with a model for either monodisperse triaxial ellipsoids with half-axes  $a$  (related to the thickness)  $< b$  (related to the width)  $< c$  (related to the length) or polydisperse rigid rods with a volume-weighted average length  $\langle L \rangle$ , relative standard deviation  $\sigma_L/\langle L \rangle$ , and an elliptical cross section with half-axes  $a$  and  $b$ . A model for polydisperse self-avoiding wormlike chains with a volume-weighted average contour length  $\langle L \rangle$ , relative standard deviation  $\sigma_L/\langle L \rangle$ , persistence length  $l_p$  and cross section half-axes  $a$  and  $b$  had to be used in order to fit the data of the samples containing the most elongated ( $\langle L \rangle \approx 900$  Å) micelles. The ribbonlike micelles formed at [SDS]:[DTAB] = 75:25 were too large for their size distribution to be determined from our SANS data. All spatial dimensions are given in angstroms (Å) and typical values of the errors of  $a$  and  $b$  are  $\pm 0.2$  Å and  $\pm 0.5$  Å, respectively. The structure factor necessary for fitting some of the data accounts for the comparatively large double-layer interactions between macroions with an effective charge  $z_{\text{eff}}$ . The ideal charge  $z_{\text{id}}$  is the charge of a micelle for which the counterions are fully dissociated. The relative standard deviation of the most polydisperse samples were found to be somewhat below unity, and in the corresponding model fits  $\sigma_L/\langle L \rangle$  was fixed to 0.95 (denoted  $\sigma_L/\langle L \rangle \approx 1$ ). All results represent data measured at Risø except  $X = 0.85$ ,  $c_{\text{surf}}^{\text{tot}} = 0.125$  and  $0.25$  wt %, which were measured at the ILL. There are good agreements between the results from the samples measured both at Risø and at the ILL despite the fact that the latter only were equilibrated 5–10 h whereas the former were equilibrated 20–25 h.

as a simple two-step function, as is expected for a monodisperse circular symmetrical cross-section consisting of an inner hydrocarbon part and an outer polar headgroup part.<sup>34</sup> A broad distribution of radii of cylindrical circular symmetric particles would give similar appearances to  $p_{\text{cs}}(R)$  and  $\Delta\rho(R)$  as for a rod with a noncircular cross-section but with the unrealistic

consequence that the largest radii of the most elongated micelles would largely exceed the length of a fully extended surfactant molecule. Moreover, previous model calculations<sup>37,38</sup> indicate that the free energy per unit length of an infinitely long cylindrical ionic micelle is a rather sharp parabolic function of the cylinder radius and, hence, a small polydispersity (about



1%) with respect to the radius is anticipated. Nor have we observed any significant polydispersity of the thickness for the various bilayer structures that form close to equimolar composition or at low surfactant concentrations [cf. Figure 1].<sup>25</sup>

A quantitative estimate of the geometrical structure of the aggregates as a function of the concentrations of anionic and cationic surfactant was obtained by means of fitting our small-angle scattering data to various models for differently shaped particles.<sup>31</sup> In accordance with the results from the model-independent inverse methods, the only models that could satisfactorily fit the data of all the samples containing micelles were models for rigid tablet-shaped or flexible ribbonlike micelles. Reasonable fits for strictly cylindrical particles consisting either of swollen end caps or two shells with different scattering length densities could only be obtained by assuming unphysical values for the end cap radius or the outer shell thickness and scattering length density, respectively.

The scattering cross-section for a monodisperse collection of interacting anisotropic particles can be expressed in the following way

$$\frac{d\sigma_m(q)}{d\Omega} = \Delta\rho_m^2 M \langle F^2(q) \rangle_0 \left[ 1 + \frac{\langle F^2(q) \rangle_0^2}{\langle F^2(q) \rangle_0} (S(q) - 1) \right] \quad (1)$$

where  $\Delta\rho_m$  is the difference in scattering length density per unit mass solute between particles and solvent and  $M$  is the molar mass of the particle. To account for interactions between the micelles, the decoupling approximation,<sup>39</sup> valid for particles with small anisotropy, was used together with a structure factor  $S(q)$  derived by Hayter and Penfold<sup>40</sup> from the Ornstein–Zernike equation and the rescaled mean spherical approximation (RMSA),<sup>41</sup> with a soft repulsive potential between two macroions surrounded by a diffuse double layer of counterions as calculated from the Poisson–Boltzmann theory. Interactions between micelles in the most diluted samples in brine appeared to be negligible and, accordingly, we could set  $S(q) = 1$  in the corresponding model fits.

The simplest model for a particle shaped as a tablet is the one for a triaxial ellipsoid with half-axes  $a$  (related to the thickness)  $< b$  (related to the width)  $< c$  (related to the length) [cf. Figure 4]. The orientational averaged form factor is obtained by means of integrating twice over the square of the amplitude

$$F(q, r) = \frac{3[\sin(qr) - qr \cos(qr)]}{(qr)^3} \quad (2)$$

where

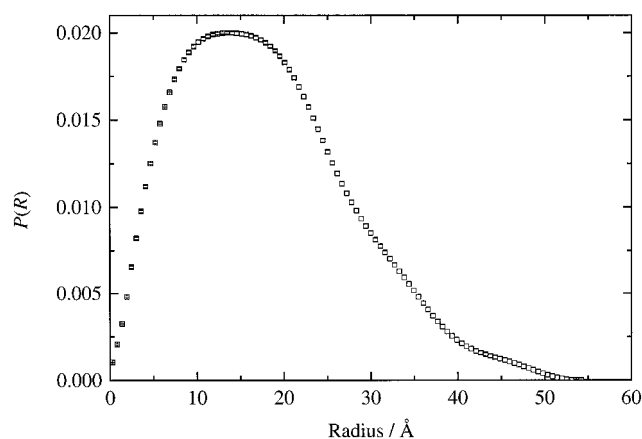
$$r(a, b, c, \phi, \theta) = \sqrt{(a^2 \sin^2 \theta + b^2 \cos^2 \theta) \sin^2 \phi + c^2 \cos^2 \phi}$$

to yield<sup>42</sup>

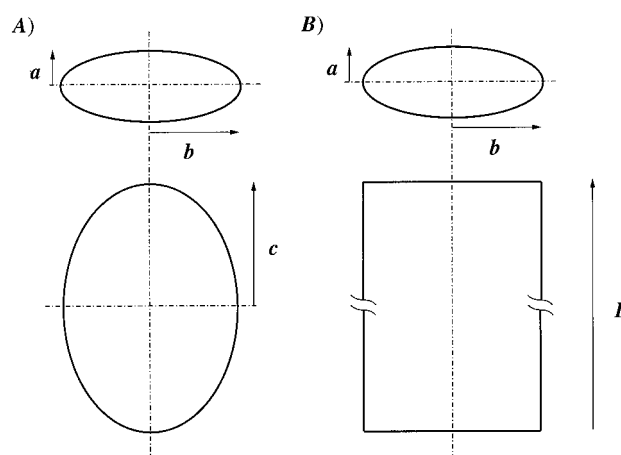
$$\langle F^2(q) \rangle_0 = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} F^2[q, r(a, b, c, \phi, \theta)] \sin \phi \, d\phi \, d\theta \quad (3)$$

$\langle F(q) \rangle_0$  is obtained in an analogous way by integration over the amplitudes. For the fitted data the agreement with the model was very good and, hence, it was not necessary to include polydispersity of either  $a$ ,  $b$  or  $c$ .

It is perhaps more realistic to model a tablet-shaped micelle as consisting of a central bilayer part surrounded by two semicylinders at the long sides and two semitoroids at the ends of the micelle. Due to the limited resolution of our scattering data, however, we cannot distinguish between this model and



**Figure 3.** Cross-section pair distance distribution function  $p(R)$  obtained by indirect Fourier transformation of a sample with a surfactant molar ratio [SDS]:[DTAB] = 80:20 at an overall surfactant concentration of 1.0 wt % in 0.1 M NaBr. The peak of  $p(R)$  corresponds well to half the thickness  $a$  and the distance where the function vanishes to the width  $2b$ , as obtained from our model fit of the same data [cf. Table 2].



**Figure 4.** Schematic representations of the model structures used for fitting the SANS data of (A) triaxial ellipsoids with half-axes  $a < b < c$  or, for sufficiently elongated micelles, a model (B) for polydisperse rods of (volume-weighted) average length  $\langle L \rangle$  with an elliptical cross-section with the half-axes denoted  $a$  and  $b$ .

one for triaxial ellipsoids and, moreover, the form factor of the former is to our knowledge not readily available and probably difficult to calculate.

In the analyses the large elongated micelles appear to be rather polydisperse with respect to the length of the micelles. To avoid unreasonably long computation times, we have simplified the model by means of separating the form factor into a part due to the length of the micelles  $P_{\text{length}}(q)$  and a part due to the particle cross section  $P_{\text{cs}}(q)$ . Hence, we have used the following scattering cross section valid for particles with a length much larger than the cross-section dimensions<sup>34</sup>

$$\frac{d\sigma_m(q)}{d\Omega} = \Delta\rho_m^2 P_{\text{length}}(q) P_{\text{cs}}(q) \langle M \rangle_w \quad (4)$$

$\langle M \rangle_w$  is the weight-average molar mass. The form factor  $P_{\text{cs}}(q)$  for an elliptical cross section with half-axes  $a$  and  $b$ , respectively, is given by

$$P_{\text{cs}}(q) = \frac{2}{\pi} \int_0^{\pi/2} \left[ \frac{2B_1(qr(a, b, \phi))}{qr(a, b, \phi)} \right]^2 d\phi \quad (5)$$

where

$$r(a,b,\phi) = \sqrt{a^2 \sin^2 \phi + b^2 \cos^2 \phi}$$

and  $B_1(x)$  is the Bessel function of first order. Since the agreement between the data and model was very good, it was not necessary to include polydispersity of the cross-section dimensions  $a$  and  $b$ .

The scattering function for polydisperse rigid rods can be written as follows

$$P_{\text{length}}(q) = \frac{\int N_{\text{rod}}(L) L^2 S_{\text{rod}}(q, L) dL}{\int N_{\text{rod}}(L) L^2 dL} \quad (6)$$

where  $N_{\text{rod}}(L)$  is the number distribution of micelles with respect to their length  $L$  and the form factor for an infinitely thin rod is given by<sup>43</sup>

$$S_{\text{rod}}(q, L) = 2\text{Si}(qL) - \frac{4 \sin^2(qL/2)}{(qL)^2} \quad (7)$$

where

$$\text{Si}(x) = \int_0^x \frac{\sin t}{t} dt \quad (8)$$

It is difficult to take interparticle interference effects into account when dealing with rather elongated micelles. However, as the long micelles only were seen to form in solutions where the intermicellar double-layer forces were negligible (micelles with comparatively low surface charge densities in brine) and, consequently, interparticle interactions were weak, we believe the model in eq 4 to be a reasonably good approximation for our purpose [see further below].

As the micelles grow beyond about 900 Å, it is evident from our scattering data that the aggregates are more or less flexible. This can be accounted for by means of using eq 4 with the modified expression

$$P_{\text{length}}(q) = \frac{\int N_{\text{worm}}(L) L^2 S_{\text{KP}}(q, L, l_p) dL}{\int N_{\text{worm}}(L) L^2 dL} \quad (9)$$

which is valid for polydisperse self-avoiding Kratky–Porod wormlike chains with a contour length  $L$  and persistence length  $l_p$ . The expressions for the scattering function  $S_{\text{KP}}(q, L, l_p)$  given by Pedersen and Schurtenberger<sup>44</sup> were used.

In our data analysis we have assumed the number density of lengths of rigid rods as well as wormlike micelles to follow a Schultz distribution

$$N_{\text{worm}}^{\text{rod}}(L) = \frac{L^z}{z!} \left( \frac{z+1}{\langle L \rangle_N} \right)^{(z+1)} e^{-L(z+1)/\langle L \rangle_N} \quad (10)$$

where  $\langle L \rangle_N$  is the number-weighted average length of the micelles. Below we have presented our results in terms of the volume-weighted average length  $\langle L \rangle = (z+2)/(z+1) \times \langle L \rangle_N$ , i.e., the mean value as calculated from the probability distribution of finding an aggregated surfactant in a micelle of length  $L$ , and the corresponding relative standard deviation  $\sigma_L/\langle L \rangle = 1/\sqrt{z+2}$ . For the most polydisperse micelles,  $\sigma_L/\langle L \rangle$  were found to be somewhat below unity with comparatively large errors and in the model fits of these samples  $\sigma_L/\langle L \rangle$  was fixed to 0.95.

**Results.** An overview of the results from our model fits for micelles formed in the absence of added salt and in 0.1 M NaBr brine is given in Tables 1 and 2, respectively. In addition to the parameters given in the tables, the molecular weight of the micelles obtained from the absolute intensities was fitted by assuming that all of the surfactants were aggregated. The last fitting parameter was a constant accounting for the residual background scattering.

When the aggregation numbers calculated from the absolute intensities, i.e., the molecular weight in our model fits, are compared with the ones obtained from the geometrical dimensions of the micelles, it is clear that the amount of surfactant that is aggregated in the micelles is less than what was added into the samples. The material loss is most evident in the DTAB-rich samples in the absence of added salt, substantially less for SDS-rich samples in pure D<sub>2</sub>O and DTAB-rich samples in brine and least for SDS-rich samples in brine. The reason for the material loss is mainly the fact that a certain amount of free surfactant monomers, slightly larger than the critical micelle concentration (cmc), is always present in the bulk solution that surrounds the surfactant aggregates so that the chemical potential of free monomers approximately equals the corresponding quantity for surfactants aggregated in the micelles. Our observations are consistent with the fact that the cmc is larger for aqueous solutions of pure DTAB (~16 mM at 25 °C in the absence of added inert salt) than for pure SDS (~8 mM). The difference in cmc between SDS and DTAB is mainly a result of the fact that the rather voluminous sulfate headgroup shields the hydrocarbon/water interface more effectively than the largely hydrophobic headgroup of DTAB. Because of the reduction of the electrostatic free energy, the free monomer concentrations are substantially reduced when either an oppositely charged surfactant or an inert salt is mixed into the micelle solutions in agreement with our observations. The formation of small amounts of a precipitate (DTA<sup>+</sup>DS<sup>-</sup>) may also contribute somewhat to the observed loss of material.

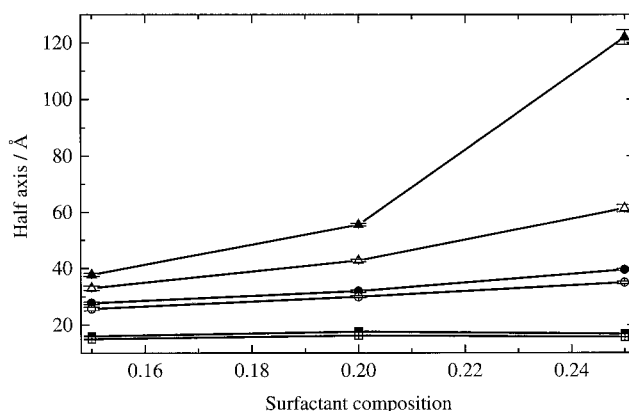
In our analyses we have subtracted the concentration of free monomers  $c_{\text{free}}$  (material loss) from the overall surfactant concentration when calculating the volume fraction of particles contributing to the intermicellar interactions taken into account by  $S(q)$  and significant improvements of the model fits were thus obtained. It is difficult to determine the ionic strength in the samples since there are unknown contributions to the electrolyte concentration from the free monomers as well as the macroionic micelles themselves and the amount of counterions that is released when two oppositely charged surfactants are mixed in a micelle. The latter is difficult to obtain since we only know the overall surfactant composition and not the composition in the micelles. In the case where no salt was added, the electrolyte concentration was simply set equal to the amount of released counterions assuming all of the surfactant to be aggregated and, where brine was used as solvent, to the amount of added salt, i.e., 0.1 M. Hence, we have neglected the contributions to the ionic strength from the free monomers as well as from the macroionic micelles themselves. We do not find it necessary to estimate the ionic strength more accurately since the errors of the values for  $z_{\text{eff}}$  obtained in the model fits are comparatively large (see further below). Moreover, the structure factor we have used has been obtained by the RMSA approximation, which is a relatively poor estimate of the electrostatic interactions. However, as the main purpose of the study is to obtain the geometrical structure of the micelles, we aim at eliminating the structure factor effects by the simple

RMSA approximation, which is easier to use than more elaborate approaches.

The aggregation number used for determining the charge of a micelle for which the counterions are fully dissociated,  $z_{id}$ , was roughly calculated from the obtained micelle volumes assuming that only the hydrocarbon  $C_{12}$  tail ( $351 \text{ \AA}^3$ ) of SDS contributes to the scattering intensity of SDS micelles whereas also the largely hydrophobic  $TA^+$  headgroup ( $109 \text{ \AA}^3$ ) of DTAB contributes to the scattering intensity of DTAB. We may note that the expected 10% error of the absolute intensities leads to a relatively large error of  $c_{free}$  and, since there is a substantial correlation between the particle volume fraction and the charge of a micelle  $z_{eff}$  in the model fits, the errors of the obtained  $z_{eff}/z_{id}$  given in Tables 1 and 2 are relatively large. Moreover, we do not know the actual composition in the micelles and have assumed it to be approximately equal to the overall surfactant composition when calculating the aggregation number and  $z_{id}$ . The difficulties of accurately determining  $z_{eff}/z_{id}$  might explain that some of its obtained values are unrealistically close to unity (and even above unity in one case) and that, according to our results,  $z_{eff}/z_{id}$  is larger at 1.0 wt % than 0.5 wt % for pure SDS micelles at  $[NaBr] = 0.1 \text{ M}$ , although the opposite is expected.<sup>45</sup> We may also stress here that  $z_{eff}$  is an effective charge as the structure factor is calculated from the PB approximation assuming, among other things, a smeared out surface charge of the micelles and infinitely small counterions (point charges) and, as a result, it is difficult to interpret what the values of  $z_{eff}/z_{id}$  physically stand for.

In the absence of added salt, we found the half-axes related to the thickness of the DTAB-rich micelles ( $16.0 \text{ \AA} \leq a \leq 18.1 \text{ \AA}$ ) to be somewhat larger than the corresponding values of the SDS-rich micelles ( $15.0 \text{ \AA} \leq a \leq 16.7 \text{ \AA}$ ). This is mainly due to the small difference in scattering length density between the sulfate headgroup and  $D_2O$  and the similarity between the trimethylammonium group and the hydrophobic tail. However, a small amount of the counterions in the diffuse layer also seems to contribute to the observed layer thicknesses as  $a$  decreased when NaBr was added ( $14.4 \text{ \AA} \leq a \leq 15.9 \text{ \AA}$  for DTAB-rich micelles and  $13.2 \text{ \AA} \leq a \leq 15.4 \text{ \AA}$  for SDS-rich micelles in 0.1 M NaBr) in accordance with a decreasing Debye length with increasing electrolyte concentration. The thickness of the micelles is substantially less than twice a fully stretched hydrocarbon  $C_{12}$  chain ( $\xi_{max} = 16.7 \text{ \AA}$ ). This is in agreement with theoretical calculations that show that the entropy contribution arising from the various accessible conformational states of the hydrocarbon chains reaches a sharp maximum for a bilayer thickness considerably less than  $2\xi_{max}$ .<sup>46,47</sup> The very same effect can also account for the observed trend in the case of added salt of decreasing  $a$  with micelle size as equimolar composition ( $X = 0.5$ ) is approached from about  $X = 0.05$  and 0.95. This is so because the thickness where the chain conformational entropy reaches its maximum decreases with geometry in the order sphere > cylinder > planar membrane.<sup>47</sup> The same trend is absent in the case where no salt was added which may be explained as a result of a counteracting influence from electrostatics tending to increase  $a$  as  $X \rightarrow 0.5$ . A dominating electrostatic free energy contribution at high surface charge densities most probably accounts for the fact that the bilayer thicknesses are smaller for pure SDS and DTAB micelles as compared with the corresponding thicknesses at  $X = 0.95$  and 0.05, respectively.

Whereas the thickness only changes slightly with the solution state, the micelles grow significantly with respect to both width and length in pure  $D_2O$  [cf. Figure 5]. The growth is most



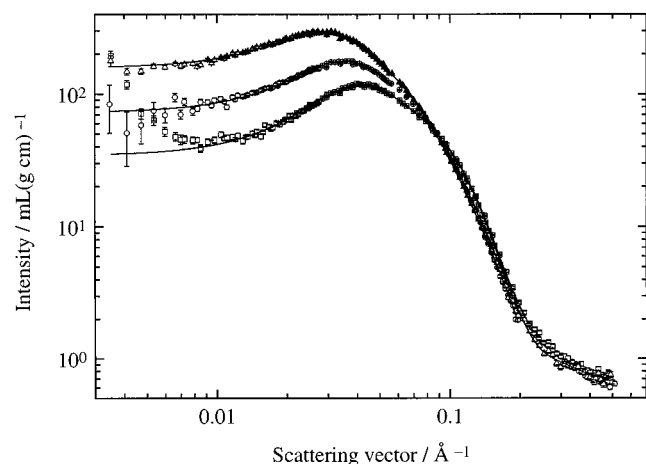
**Figure 5.** Half-axes related to the thickness  $a$  (squares), width  $b$  (circles), and length  $c$  (triangles), with error bars, plotted against the surfactant compositions  $X \equiv [SDS]/([SDS] + [DTAB])$  for DTAB-rich micelles (solid symbols) and  $1 - X$  for SDS-rich micelles (open symbols) at an overall surfactant concentration of 1.0 wt % in the absence of added salt. Both length and (to a less extent) width increase significantly as the equimolar composition is approached.

evident when the surfactant composition  $X \equiv [SDS]/([SDS] + [DTAB])$  approaches the equimolar composition ( $X = 0.5$ ) for a given surfactant concentration  $c_{surf}^{tot} \equiv [SDS] + [DTAB]$ , but there is also a slight trend of increasing micelle size with decreasing  $c_{surf}^{tot}$  for a given  $X$  at low surfactant concentrations. The half-axis related to the width  $b$  increases from about 25 to 45 Å and  $c$  (related to the length) increases from about 35 to 160 Å [cf. Figure 5 and Table 1]. When the surfactant composition further approaches equimolarity at  $c_{surf}^{tot}$  above about 0.5 wt % (DTAB-rich samples) or  $c_{surf}^{tot}$  above about 0.25 wt % (SDS-rich samples), an abrupt transition, at  $X \approx 0.30$  and 0.70, from micelles to large lamellar sheets occurs, and when samples containing micelles are diluted below about 0.5 wt % (DTAB-rich samples) or 0.25 wt % (SDS-rich samples), for a given  $X$ , we observe a transition from micelles to vesicles [cf. Figure 1a].

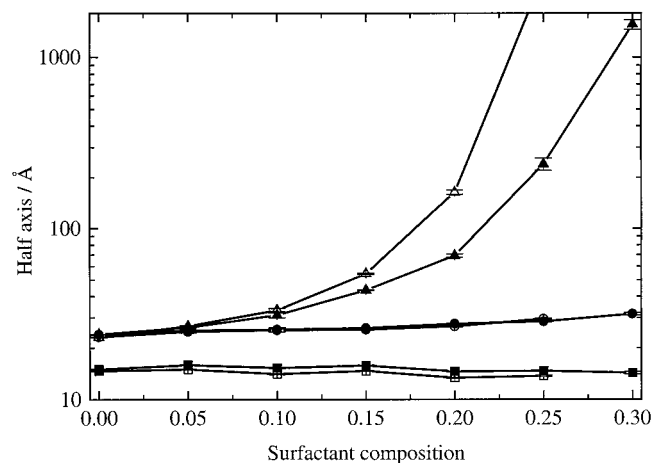
Examples of scattering data, together with model fits, for SDS-rich samples containing micelles in the absence of added salt for different surfactant compositions  $X$  at a given overall surfactant concentration  $c_{surf}^{tot} = 1.0 \text{ wt %}$  are given in Figure 6. A difference in the scattering behavior can be observed in the range that contains information about the cross-section dimensions of the micelles ( $q \approx 0.1$ ) as the cross section ellipticity of the micelles is changed upon increasing the width at an approximately constant thickness. The size of the micelles is approximately given by the  $q$  value where the intensity begins to decrease with increasing  $q$ , and the comparatively large double-layer interaction between the micelles in the absence of added salt accounts for the conspicuous reduction of the intensity at the lowest  $q$  values giving rise to evident peaks in all the scattering data given in Figure 6.

Pure SDS as well as DTAB micelles appear to be shaped as small disks or oblate ellipsoids of revolution in 0.1 M NaBr. This is a somewhat unexpected discovery and contradicts the general belief that SDS form spherical micelles in the absence of added salt, which grow in the length direction into cylinders as an external salt is added. It has, however, previously been argued that SDS form oblate rather than prolate micelles in 0.1 M NaCl at 25°C. In a forthcoming paper we will in more detail present an investigation of the geometrical structure of pure SDS and DTAB micelles formed at different concentrations of added salt.<sup>49</sup> The bilayer radius of the disk-shaped micelles increases from about 23 Å (SDS micelles) and 24 Å (DTAB micelles) to



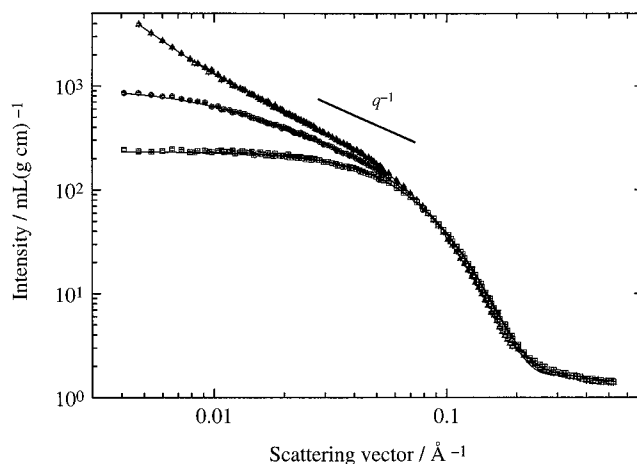


**Figure 6.** Normalized scattering intensity as a function of scattering vector  $q$  for samples with a surfactant molar ratio [SDS]:[DTAB] = 85:15 (squares), 80:20 (circles), and 75:25 (triangles) at an overall surfactant concentration of 1.0 wt % in the absence of added salt. Individual symbols represent data obtained with different combinations of neutron wavelength and sample–detector distance. The lines represent the results from fits with models for monodisperse triaxial ellipsoids. The results of the model fits are given in Table 1. The agreements of the fits as measured by  $\chi^2$  are 2.9 ([SDS]:[DTAB] = 85:15), 5.3 ([SDS]:[DTAB] = 80:20), and 2.2 ([SDS]:[DTAB] = 75:25).



**Figure 7.** Half-axes related to the thickness  $a$  (squares), width  $b$  (circles), and length  $c$  (triangles), with error bars, of micelles formed at an overall surfactant concentration of 1.0 wt % in 0.1 M NaBr plotted against the surfactant compositions  $X \equiv [\text{SDS}]/([\text{SDS}] + [\text{DTAB}])$  for DTAB-rich micelles (solid symbols) and  $1 - X$  for SDS-rich micelles (open symbols). For the polydisperse micelles formed at  $20:80 \leq [\text{SDS}]:[\text{DTAB}] \leq 80:20$  the (triangular) symbols represent half the volume-weighted average length  $\langle L \rangle/2$ . Note the logarithmic scale of the vertical axis.

25 and 26 Å at  $X = 0.95$  and 0.05, respectively. As equimolar composition is further approached for a given  $c_{\text{surf}}^{\text{tot}}$  the micelles formed in a 0.1 M NaBr solution, in striking contrast to the case where no extra salt was added, grow much stronger with respect to the length than to the width [cf. Figure 7]. The half-axis  $b$  (related to the width) of the micelles increases to about 30 Å ( $X = 0.30$  and 0.75) whereas the length, of the DTAB-rich micelles, increases to  $\langle L \rangle \approx 3000$  Å ( $X = 0.30$ ). The largest SDS-rich micelles, found at  $X = 0.75$ , were so long (i.e., several thousands of Ångströms) that we cannot determine their size distribution ( $\langle L \rangle$  and  $\sigma_L/\langle L \rangle$ ) from our SANS data. When the micelles become sufficiently elongated, i.e. above about 900 Å, they appear to be shaped as flexible ribbons with a persistence length  $60 \text{ Å} < l_p < 220 \text{ Å}$ . We have indicated in the ternary

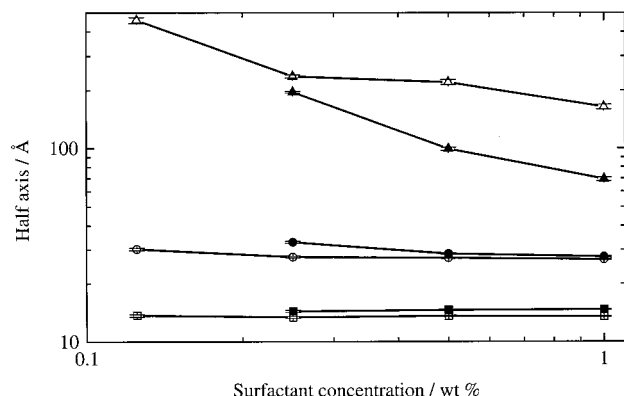


**Figure 8.** Normalized scattering intensity as a function of the scattering vector  $q$  for samples with a surfactant molar ratio [SDS]:[DTAB] = 85:15 (squares), 80:20 (circles), and 75:25 (triangles) at an overall surfactant concentration of 1.0 wt % in 0.1 M NaBr. Individual symbols represent data obtained with different combinations of neutron wavelength and sample–detector distance. The lines represent the results from fits with models for monodisperse triaxial ellipsoids (squares), polydisperse rigid rods with an elliptical cross-section (circles), and self-avoiding wormlike ribbons with an elliptical cross-section (triangles). The results of the model fits are given in Table 2. The agreements of the fits as measured by  $\chi^2$  are 4.3 ([SDS]:[DTAB] = 85:15), 5.5 ([SDS]:[DTAB] = 80:20), and 5.5 ([SDS]:[DTAB] = 75:25).

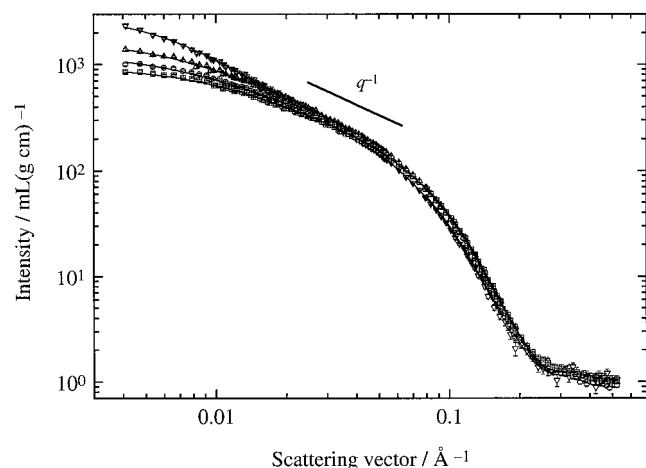
diagram in Figure 1b the regime wherein the data from the samples had to be fitted with a model for flexible wormlike micelles (ribbons) rather than with a model for rigid rods (tablets). The polydispersity increases with decreasing  $c_{\text{surf}}^{\text{tot}}$  (and increasing size of the micelles) in samples where  $X = 0.15$ , 0.25, and 0.85, whereas, in contrast to theoretical expectations, it decreases upon diluting the samples when  $X = 0.20$  and 0.80 [cf. Table 2]. Perhaps the omission of a structure factor in the data analyses of the substantially elongated rods influences the results from our model fits. The volume-weighted relative standard deviation for the most polydisperse, rigid as well as flexible, micelles appeared to be close to unity. This corresponds to an exponent equal to  $z = -1$  in the number distribution in eq 10, and a ratio  $\langle L_N \rangle / \langle L \rangle$  approaching infinity, as is expected for an exponential distribution using a Flory–Huggins-like expression (that is with volume fraction rather than mole fraction) for the entropy of mixing particles and solvent.

Examples of scattering data, together with model fits, for SDS-rich samples containing micelles in 0.1 M NaBr at different surfactant compositions  $X$  and a given overall surfactant concentration  $c_{\text{surf}}^{\text{tot}} = 1.0$  wt % are given in Figure 8. The data virtually coincide in the cross-section region of the scattering vector ( $q \approx 0.1$ ) as both thickness and width increases only very slightly with  $X$ . For rigid rods, the scattering intensity varies as  $q^{-1}$  at intermediate  $q$  values whereas the magnitude of the slope is larger for the flexible wormlike chains. For the latter, there is a crossover to a  $q^{-1}$  dependence as the  $q$  value corresponding to  $\sim l_p^{-1}$  is reached, giving rise to a point of inflection in the log–log plot of  $I(q)$  for ribbonlike micelles with  $\langle L \rangle \gg l_p$ . The slope of  $\log I$  as a function of  $\log q$  in the medium  $q$  range for the  $X = 0.80$  sample is not strictly linear, but rather curved, as a result of the large polydispersity in the length direction of these micelles. The intensity becomes constant with respect to the scattering vector for  $q$  values lower than about the inverse of the radius of gyration of the micelles.

As a result of a free monomer effect (see further below), there is for the samples in which brine was used as solvent a clear



**Figure 9.** Half-axes related to the thickness  $a$  (squares), width  $b$  (circles), and half the volume-weighted average length  $\langle L \rangle/2$  (triangles), with error bars, of micelles formed at a surfactant composition [SDS]:[DTAB] = 80:20 in 0.1 M NaBr plotted against the overall surfactant concentration  $c_{\text{surf}}^{\text{tot}}$  for SDS-rich micelles (open symbols) and DTAB-rich micelles (solid symbols). Note the logarithmic scales of both axes.



**Figure 10.** Normalized scattering intensity as a function of the scattering vector  $q$  for samples with an overall surfactant concentration [SDS] + [DTAB] = 1.0 wt % (squares), 0.50 wt % (circles), 0.25 wt % (up triangles), and 0.125 wt % (down triangles) at a surfactant composition [SDS]:[DTAB] = 80:20 in 0.1 M NaBr. Individual symbols represent data obtained with different combinations of neutron wavelength and sample–detector distance. The lines represent the results from fits with models for polydisperse rigid rods with an elliptical cross-section (squares, circles and up triangles) and self-avoiding wormlike ribbons with an elliptical cross-section (down triangles). Note the deviation from a  $q^{-1}$  behavior in the linear regime of the data fitted with a model for wormlike micelles. The results of the model fits are given in Table 2. The agreements of the fits as measured by  $\chi^2$  are 5.5 (1.0 wt %), 3.3 (0.5 wt %), 2.2 (0.25 wt %), and 1.1 (0.125 wt %).

increase in micelle size with decreasing  $c_{\text{surf}}^{\text{tot}}$  [cf. Figure 9 and Table 2]. The same effect was observed for the samples in which no salt was added [cf. Table 1], except for the highest values of  $c_{\text{surf}}^{\text{tot}}$ . As was the case when  $X \rightarrow 0.5$  at constant  $c_{\text{surf}}^{\text{tot}}$ , the growth of the micelles in brine occurs almost exclusively in the length direction whereas in the absence of added salt they grow significantly both with respect to width and length. Examples of scattering data, together with model fits, for SDS-rich samples containing micelles in 0.1 M NaBr at different surfactant concentrations  $c_{\text{surf}}^{\text{tot}}$  at a given surfactant composition  $X = 0.80$  are given in Figure 10. The large elongated micelles in the most diluted sample ( $c_{\text{surf}}^{\text{tot}} = 0.125$  wt %) appear to be flexible rather than rigid and, hence, the scattering intensity declines with a different slope in the linear regime as compared with the rigid rods. The flexible micelles at  $X = 0.80$

and 0.125 wt % are also slightly wider than the rigid rods at higher  $c_{\text{surf}}^{\text{tot}}$ , which is seen in Figure 10 from the different scattering behavior in the cross-section region at  $q \approx 0.1 \text{ Å}^{-1}$ .

We have not included any interparticle interactions in the analyses of the data of the rather elongated micelles formed at  $0.20 \leq X \leq 0.25$  and  $0.75 \leq X \leq 0.80$  in brine, as model expressions are not available for a collection of considerably polydisperse and anisotropic particles. However, from the results of  $\langle L \rangle$  obtained in our model fits we can roughly estimate<sup>50</sup>  $S(0)^{-1}$  to be about 1.35 for  $X = 0.80$  and  $c_{\text{surf}}^{\text{tot}} = 1.0$  wt %, the value of which decreases upon further diluting the samples. This corresponds to a difference between  $\langle L \rangle$  as obtained from our model fits and the real value of less than about 15%. Hence, the neglect of interparticle interference effects may affect the quantitative outcome of our analyses as to the length and persistence length of large elongated micelles but cannot influence the observed trends of increasing micelle size with decreasing  $c_{\text{surf}}^{\text{tot}}$ .

## Discussion

As we have studied micelles that are mixed by two oppositely charged surfactants with *identical hydrocarbon parts*, the micelle size and shape as a function of the surfactant composition in the micelle must exclusively be an effect originating from the difference in headgroups between the two surfactants. The incomparably most important contribution to the geometrical dependence of the free energy of a charged micelle that is associated with the headgroups is due to electrostatics. This means that the growth of micelles as their surfactant composition approaches 0.5 can be rationalized as an effect of decreasing surface charge density of the micelles as an increasing amount of the charges are canceled when pairs of an anionic and a cationic surfactant are aggregated and the corresponding counterions are released into the surrounding bulk solution. The effect (mainly entropic) of locating the headgroup charges, with an adjacent diffuse double-layer of counterions, at the surfaces of the micelles gives rise to a large unfavorable contribution to the free energy of forming a charged surfactant micelle. As the entropy of the counterions is a strong function of the volume they occupy, substantially charged surfactant aggregates tend to curve their interfaces in order to spread out its counterions and form relatively small micelles. The curvature of the micelles decreases (i.e., the size of the micelles increases) as the magnitude of the electrostatic free energy is reduced by means of increasing the electrolyte concentration or decreasing the surface charge density of the micelles.

Hence, we were able to observe an increasing size of the micelles as a result of either decreasing surface charge density as  $X \rightarrow 0.5$  or using 0.1 M NaBr rather than pure D<sub>2</sub>O as solvent. A decreasing surface charge density of the surfactant aggregates, resulting in the observed micelle growth with decreasing  $c_{\text{surf}}^{\text{tot}}$  [cf. Tables 1 and 2], is also obtained when a sample, at low surfactant concentrations, is diluted while  $X$  is kept fixed. The observed trend can be rationalized by considering the fact that a certain amount of surfactants exists as free monomers in the bulk solution, the concentrations of which are determined by the chemical potentials,  $\mu_{\text{SDS}}^{\text{free}} \approx \langle \mu_{\text{SDS}}^{\text{mic}} \rangle \propto \ln c_{\text{SDS}}^{\text{free}}$  and  $\mu_{\text{DTAB}}^{\text{free}} \approx \langle \mu_{\text{DTAB}}^{\text{mic}} \rangle \propto \ln c_{\text{DTAB}}^{\text{free}}$ , respectively, where  $\langle \mu_{\text{SDS}}^{\text{mic}} \rangle$  and  $\langle \mu_{\text{DTAB}}^{\text{mic}} \rangle$  are the average chemical potentials of SDS and DTAB aggregated in the micelles. The unfavorable electrostatic work of bringing extra charge, i.e., the surfactant in excess, to the micelle surface is several orders of magnitude higher than the corresponding work of bringing the surfactant in deficit into a micelle and reducing its surface charge as an effect of cancelation. In other

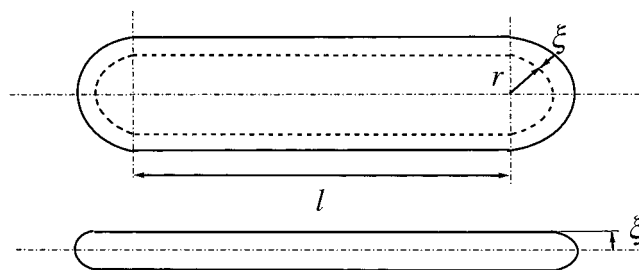
words, the free monomer chemical potential of the surfactant in excess  $\mu_{\text{excess}}^{\text{free}}$  is always much larger than the corresponding value  $\mu_{\text{deficit}}^{\text{free}}$  for the surfactant in deficit (except for values of  $X$  close to 0.5). Previous model calculations on vesicles formed from a mixture of an anionic and a cationic surfactant<sup>51</sup> indicate that the ratio  $c_{\text{excess}}^{\text{free}}/c_{\text{deficit}}^{\text{free}}$  can be as large as  $10^5$ – $10^7$ , depending on the composition in the aggregates. These values are also consistent with the results of an extremely low concentration of free DTA<sup>+</sup> in SDS-rich samples observed by Kamenka et al. in a potentiometry study with a DTA<sup>+</sup> ion specific electrode for the SDS/DTAB/H<sub>2</sub>O system at 30°C.<sup>15</sup> Hence, virtually all free monomers in the bulk solution are surfactants in excess, which means that, when a mixed surfactant solution is diluted at a fixed  $X$  and the fraction of surfactants in the free monomer state increases, the fraction of surfactants in excess that are aggregated in the micelles *decreases* and so does the surface charge density of the micelles.

As a result of the free monomer effect, SDS-rich as well as DTAB-rich micelles, following a path of dilution from about  $c_{\text{surf}}^{\text{tot}} = 1.0$  wt % for a given  $X$ , grow in size as their surface charge densities decreases. Eventually, a transition occurs to either unilamellar vesicles with a size that grows upon further dilution or, in some of the samples in which brine was used as solvent, stacks of lamellar sheets. The micelle-to-vesicle transition occurs in the DTAB-rich samples at approximately twice the overall surfactant concentration as compared with the SDS-rich samples, in accordance with the difference with a factor 2 in cmc between the two surfactants [cf. Figure 1]. Upon further dilution, an increasing amount of a precipitate (DTA<sup>+</sup>DS<sup>−</sup>) is formed in the absence of added salt as well as in 0.1 M NaBr, just as is the case when the overall surfactant composition approaches equimolarity beyond about  $X = 0.40$  and 0.60. A changing composition in surfactant aggregates with increasing concentration for fixed values of the overall surfactant composition, as well as a transition from vesicles to micelles, has recently been observed by Villeneuve et al. in surface tension measurements of mixtures of sodium decyl sulfate and decyltrimethylammonium bromide at 25°C.<sup>52</sup>

When extra salt is added to the surfactant solutions and becomes mixed into the diffuse layers of counterions outside each micelle,  $\langle \mu_{\text{excess}}^{\text{mic}} \rangle$  is lowered and, as a result, there is a transfer of free monomers (surfactants in excess) into the aggregates. The resulting increase of the surface charge density, together with the fact that the work of bending a planar bilayer into a geometrically closed vesicle increases sharply with electrolyte concentration,<sup>53,51</sup> accounts for the observed destabilization of vesicles, and the formation of either micelles or lamellar sheets, upon addition of NaBr to the mixed surfactant solutions [cf. Figure 1].

The persistence length of the flexible ribbonlike micelles was observed to increase from  $l_p = 99$  Å at  $X = 0.75$  and 0.25 wt % to  $l_p = 208$  Å at  $X = 0.80$  and 0.125 wt % as a result of the increase in surface charge density of the micelles. The observed increase of  $l_p$  with  $c_{\text{surf}}^{\text{tot}}$  for the very long ribbonlike micelles formed at  $X = 0.75$  is partly also a result of the same effect, although the absence of a structure factor in the corresponding model fits may have influenced the quantitative results for  $l_p$  [cf. Table 2].<sup>50</sup>

At higher surfactant concentrations, when the amounts of free monomers are negligible as compared with the number of surfactants that are aggregated in the micelles, an *increasing* size of the micelles is expected as the total surfactant concentration is raised for a given  $X$ , just as is the case for pure surfactant aggregates.<sup>54</sup> The magnitude of this kind of micellar growth is



**Figure 11.** Tablet-shaped micelle modeled as consisting of a central rectangular bilayer of thickness  $2\xi$ , width  $2r$ , and length  $l$  with two half-circular ends with radius  $r$ . The bilayer part is surrounded by two straight half-cylindrical rims of length  $l$  and radius  $\xi$  along the central rectangular part and two half-toroids of radius  $\xi$  along the half-circular ends of the micelle.

determined by the chemical potential related to the work of inserting an *additional surfactant* in a micelle as compared with the chemical potential related to the work per aggregated monomer of forming an *additional micelle*.<sup>55,56</sup>

**Thermodynamics of Tablet-Shaped Micelles.** We have argued above that the increasing size of the surfactant micelles we have observed can be qualitatively understood as an effect basically arising from a change of the electrostatic contribution to the free energy of forming the aggregates. However, more sophisticated arguments have to be employed in order to rationalize for the peculiar observation that the growth of tablet-shaped micelles in 0.1 M NaBr is much stronger in length than in width as compared with micelles formed in pure D<sub>2</sub>O. An indication toward a solution of the problem may be given considering a tablet-shaped surfactant micelle as consisting of three different geometrical parts [cf. Figure 11]: (i) a central bilayer consisting of a rectangle of length  $l$  and width  $2r$  with two half-circular parts of radius  $r$  at each short side surrounded by (ii) two straight half-cylindrical rims of length  $l$  along each long side and (iii) two half-toroids at the ends of the micelle. The free energy of a single micelle can then be written as a sum of contributions from the various geometrical parts<sup>57</sup>

$$\epsilon_{\text{tablet}} = A_{\text{tor}}\gamma_t + A_{\text{bil}}\gamma_{\infty}^b + A_{\text{cyl}}\gamma_{\infty}^c \quad (11)$$

where  $A_{\text{tor}} = 2\pi\xi(\pi r + 2\xi)$ ,  $A_{\text{cyl}} = 2\pi\xi l$ , and  $A_{\text{bil}} = 2r(\pi r + 2l)$  are the areas of the toroidal, straight cylindrical, and planar parts, respectively.  $\xi$  is the half-thickness of the bilayer part of the micelle, equal to the radial thickness of the rims, that minimizes  $\epsilon_{\text{tablet}}$ .  $\gamma_{\infty}^c$  and  $\gamma_{\infty}^b$  are the free energies, minimized with respect to the surfactant composition, per unit area of forming an infinitely straight cylinder and an infinitely large bilayer sheet, respectively, out of monomers in the surrounding bulk solution. The corresponding quantity for a convexly bent half-toroid can be approximated with an expansion to second order in curvature of the rim

$$\gamma_t = \gamma_{\infty}^c + k_1/(r + \xi) + k_2/(r + \xi)^2 \quad (12)$$

and, hence, we can write the overall free energy of forming a tablet-shaped micelle out of its constituent monomers as a function of its width and length as follows

$$\epsilon_{\text{tablet}}(r, l) = \frac{\alpha_1}{r + \xi} + \alpha_0 + 2\pi\xi(\pi r + l)\gamma_{\infty}^c + 2r(\pi r + 2l)\gamma_{\infty}^b \quad (13)$$

Here  $\alpha_1 = 2\pi\xi[\pi k_2 - \xi k_1(\pi - 2)]$  and  $\alpha_0 = 2\pi^2\xi k_1$  are constants (insofar as  $\xi$  varies only slightly with  $r$ ) related to the bending free energy of the toroidal end caps of the micelles.



The various free energy contributions related to electrostatics, headgroups, and hydrocarbon tails of the surfactants all contribute to the actual values of the bending constants in a similar way as they do for the bilayer bending work of vesicles (see further below).<sup>51,53</sup>

The size distribution, expressed as a volume fraction density,<sup>38,58</sup> is obtained by

$$\phi(r, l) = C(r) e^{-\epsilon_{\text{tablet}}(r, l) kT} \quad (14)$$

where  $C(r)$  is a prefactor arising from a change of variables from aggregation numbers in the various geometrical parts of the micelle to  $r$  and  $l$ .<sup>57,59</sup> We may note that  $\epsilon_{\text{tablet}}$  must always be larger than zero in order to account for an overall volume fraction of micelles less than 1. The average width and length of polydisperse tablet-shaped micelles can then be obtained from eqs 13 and 14 using the following expressions

$$\langle r \rangle = \frac{\int_0^\infty \int_0^\infty r \phi(r, l) dr dl}{\int_0^\infty \int_0^\infty \phi(r, l) dr dl} \quad (15)$$

and

$$\langle l \rangle = \frac{\int_0^\infty \int_0^\infty l \phi(r, l) dr dl}{\int_0^\infty \int_0^\infty \phi(r, l) dr dl} \quad (16)$$

According to eqs 13–16, the average width and length of a tablet-shaped micelle are determined by the magnitudes of the free energies of the three geometrical parts of the micelle. The parameters related to the bending free energy of the end cap rims  $\alpha_1$  and  $\alpha_0$  as well as the cylinder and bilayer tensions,  $\gamma_\infty^c$  and  $\gamma_\infty^b$  respectively, are all functions of the surfactant composition in the concerned geometrical part as well as of electrolyte concentration and temperature. The absolute values of  $\gamma_\infty^c$  and  $\gamma_\infty^b$  are determined by a condition for a given overall surfactant concentration  $\phi_{\text{surf}}^{\text{tot}}$ . The latter is obtained by means of integrating eq 14 over all  $r$  and  $l$  and adding the resulting value for the volume fraction of free monomers  $\phi_{\text{free}}$ , which is implicitly included in  $\gamma_\infty^c$  and  $\gamma_\infty^b$ , so  $\phi_{\text{surf}}^{\text{tot}} = \phi_{\text{mic}} + \phi_{\text{free}}$ .<sup>13</sup> Hence, for a given overall surfactant concentration the average length and width of the micelles can be calculated from eqs 13–16 for a given set of values of  $\alpha_1$ ,  $\alpha_0$ , and  $\gamma_\infty^c/\gamma_\infty^b$ . The thermodynamic parameters can be expressed in terms of the various contributions to the overall free energy of forming a surfactant aggregate, of which mainly electrostatics is responsible for the variation of  $\alpha_1$ ,  $\alpha_0$ , and  $\gamma_\infty^c/\gamma_\infty^b$  with composition of an anionic and a cationic surfactant with identical hydrocarbon parts. More curved structures are favored by the large negative contribution to  $\alpha_0$  from electrostatics and, as it vanishes (and  $\alpha_0$  increases) with decreasing surface charge density as equimolar composition is approached, the micelles become larger. The positive quantities  $\gamma_\infty^c$  and  $\gamma_\infty^b$  both approach zero as the magnitude of  $\alpha_0$  increases as a consequence of the condition of fixed overall surfactant concentration.

Moreover, the higher order bending constant  $\alpha_1$  appears to be crucial for the determination of the degree of rodlikeness or disklikeness of the micelles. This is so because the last term in eq 13 ( $=4\gamma_\infty^b r l$ ), including both  $r$  and  $l$ , influences the width and length distribution of the micelles so that small values of  $r$  are favored for large values of  $l$  and vice versa.<sup>57</sup> Hence, small values of  $\alpha_1$  (including negative values) favor rodlike micelles

whereas higher values of  $\alpha_1$  favor the formation of more disklike micelles for which the rim is less bent.

Most interestingly, eq 13 is a generalization of the corresponding expression for a strictly circular disk-shaped micelle and the same thermodynamic parameters ( $\alpha_0$ ,  $\alpha_1$ ,  $\gamma_\infty^c$ , and  $\gamma_\infty^b$ ) determine the free energy of a tablet-shaped and a disk-shaped micelle, respectively. This means, in accordance with eqs 13–16, that micelles shaped as bilayer fragments in general are more or less elongated for a given set of values of the thermodynamic parameters. Strictly, disk-shaped micelles are only obtained as a special case when  $\langle l \rangle \approx 0$  which becomes true for large values of  $\alpha_1$ . In addition,  $\gamma_\infty^c/\gamma_\infty^b$  also influences the  $l$ -to- $r$  ratio of the micelles.

For sufficiently large values of  $\alpha_0 + \alpha_1/(r + \xi)$ ,  $\gamma_\infty^b$  turns negative as a result of the condition of a given overall surfactant concentration, and the free energy given by eq 13 obtains a maximum for some finite values of  $r$  and  $l$  and its lowest value for  $r = l = \infty$ . Hence, at the surfactant composition where  $\gamma_\infty^b = 0$ , an abrupt transition from micelles to huge lamellar sheets is expected unless the samples are sufficiently diluted to enable the formation of vesicles.<sup>22</sup> A transition from micelles to stacks of lamellar sheets as well as to vesicles as the surface charge density of the aggregates decreases beyond a certain level was clearly observed in our experiments [cf. Figure 1].

## Concluding Remarks

Traditionally, surfactant micelles have been roughly divided into three categories: linear rodlike micelles, two-dimensional disklike micelles, and three-dimensional spherical symmetrical micelles. However, the anisotropic micelles we have found in aqueous mixtures of an anionic and a cationic surfactant do not grow in either one or equally in two directions with changing surface charge density. On the contrary, small disklike micelles grow asymmetrically with respect to width and length into elongated tablets and flexible ribbons. In the absence of added salt mixed SDS/DTAB tablet-shaped micelles appear to behave more like disks (i.e., they grow significantly with respect to both width and length), whereas in 0.1 M NaBr brine the micelles appear to be more rodlike (i.e., they grow much stronger in length than in width). As a result, micelles at a given solution state appear to have a single well-defined structure and any coexistence between fundamentally differently shaped micelles such as spheres, cylinders, and disks could not be observed. The coexistence between micelles and vesicles was, however, evident in several of the investigated samples.<sup>25</sup>

The thermodynamic parameters  $\alpha_1$ ,  $\alpha_0$ , and  $\gamma_\infty^c/\gamma_\infty^b$  can be calculated from a model as functions of the solution state for mixtures of an anionic and a cationic surfactant in a way similar to that previously done for the bending and stretching work of unilamellar vesicles.<sup>51,53</sup> The free energies of forming the various geometrical parts of a micelle can be divided into several contributions<sup>13,38</sup> of which the hydrophobic effect and electrostatics appear to be more important than the others. The former can be calculated as the work of bringing hydrocarbon chains from an aqueous solution to an  $n$ -alkane bulk phase added with the contribution due to the residual hydrocarbon/water interfacial tension,<sup>1</sup> whereas the latter is calculated as the work of charging the micelle surface outside which a diffuse layer of counterions is located. As the surfactants in our investigation have identical hydrocarbon parts, the composition in the various geometrical parts of a micelle only influence free energy contributions attributed to the headgroups. Moreover, the observed symmetrical behavior with respect to SDS-rich and DTAB-rich aggregates indicates that the influence from free energy



contributions associated with the headgroups other than electrostatics is small. The free energy contribution of a diffuse layer of monovalent counterions outside a charged surface can be explicitly calculated from the Poisson–Boltzmann (PB) mean-field theory.<sup>60,61</sup> Hence, a very interesting task is to find out whether the PB theory incorporated in the kind of model calculations described above can account for the observed different trends of micelle growth in the absence of added salt and in 0.1 M NaBr, respectively, which has been experimentally demonstrated in the present paper.

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