Formation of Tablet-Shaped and Ribbonlike Micelles in Mixtures of an Anionic and a Cationic Surfactant

2 AUTHORS:

Magnus Bergstrom
Uppsala University

62 PUBLICATIONS   **1,568** CITATIONS

SEE PROFILE

Jan Skov Pedersen
Aarhus University

363 PUBLICATIONS   **10,991** CITATIONS

SEE PROFILE

Formation of Tablet-Shaped and Ribbonlike Micelles in Mixtures of an Anionic and a Cationic Surfactant

Magnus Bergström* and Jan Skov Pedersen

Condensed Matter Physics and Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

SANS experiments demonstrate the formation of tablet-shaped micelles in aqueous mixtures of an anionic (SDS) and a cationic (DTAB) surfactant. The micelles grow in size as equimolar composition is approached at a given surfactant concentration or when the mixtures are diluted at low concentrations at a given surfactant composition. In the absence of added salt, both the width and the length of the micelles increase significantly, whereas, using 0.1 M NaBr brine as a solvent, the micelles grow dramatically in length but only very slightly in width. As a result, ribbonlike micelles as long as several thousand angstroms form in the latter case.

Introduction

A change in the geometry of surfactant aggregates can be induced by means of adding a third component to a binary surfactant in water solution, for example, a conventional salt[1−3] or a nonionic cosurfactant,[4−7] that influences the electrostatics of the system. Structural changes also occur when two spherical micelle-forming surfactants with opposite charges (e.g. the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic surfactant dodecyl trimethylammonium bromide (DTAB)) are mixed in certain proportions in aqueous solutions. A variety of equilibrium microstructures, including small globular as well as large wormlike micelles, rather small unilamellar vesicles, and large lamellar sheets, have been demonstrated in several recent studies of aqueous anionic/cationic surfactant mixtures.[8−14]

In a recent paper,[14] we have presented the various microstructures found in mixtures of SDS and DTAB in pure (heavy) water at 40 °C using small-angle neutron scattering (SANS) (cf. Figure 1a). Above the concentration where vesicles do not form, our data were fitted by various geometrical models. This gave the following transition series as equimolar composition was approached for a given overall surfactant concentration: cylindrical rods
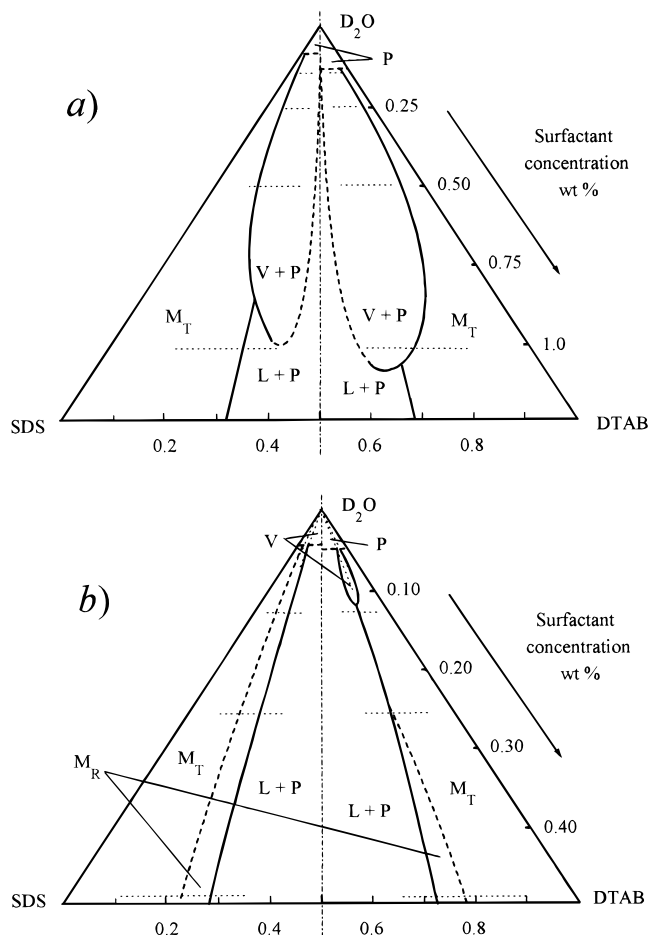
Figure 1. Ternary diagrams showing the regimes of different microstructures found at 40 °C in mixtures of SDS and DTAB using either (a) pure D_2O or (b) 0.1 M NaBr in D_2O as solvent. Several samples along the dotted lines were measured. Uni- or oligolamellar vesicles (V), rigid tablet-shaped micelles (M_T), and stacks of lamellar sheets (L) are found. In the most dilute parts, a precipitate (P) of DTA^+DS^- is formed. For 0.1 M NaBr, the micelles are able to become so long that they are flexible ribbonlike micelles (M_R). Note the different scales for the two diagrams of the axes denoting the surfactant concentration.

with swollen end caps → polydisperse oblate ellipsoids of revolution → lamellar bilayer sheets. In the present paper, however, we present recent unexpected results for micelles

* Corresponding author. Telephone: +45 46 77 47 45. Fax: +45 46 77 47 90. E-mail: magnus@risoe.dk.

(1) Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075.
(2) Söderman, O.; Jonströmer, M.; van Stam, J. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1759.
(3) Törnblom, M.; Henriksson, U.; Ginley, M. *J. Phys. Chem.* **1994**, *98*, 7041.
(4) Hargreaves, W. R.; Deamer, D. W. *Biochemistry* **1978**, *17*, 3759.
(5) Backlund, S.; Rundt, K.; Veggeland, K.; Høiland, H. *Prog. Colloid Polym. Sci.* **1987**, *74*, 93.
(6) Hervé, P.; Roux, D.; Bellocq, A.-M.; Nallet, F.; Gulik-Krzywicki, T. *J. Phys. II* **1993**, *3*, 1255.
(7) Hoffmann, H.; Munkert, U.; Thunig, C.; Valiente, M. *J. Colloid Interface Sci.* **1994**, *163*, 217.
(8) Kamenka, N.; Chorro, M.; Talmon, Y.; Zana, R. *Colloids Surf.* **1992**, *67*, 213.
(9) Kaler, E. W.; Herrington, K. L.; Murthy, A. K.; Zasadzinski, J. A. N. *J. Phys. Chem.* **1992**, *96*, 6698.
(10) Herrington, K. L.; Kaler, E. W.; Miller, D. D.; Zasadzinski, J. A. N.; Chiruvolu, S. *J. Phys. Chem.* **1993**, *97*, 13792.
(11) Marques, E.; Khan, A.; Miguel, M. G.; Lindman, B. *J. Phys. Chem.* **1993**, *97*, 4729.
(12) Talhout, R.; Engberts, J. B. F. N. *Langmuir* **1997**, *13*, 5001.
(13) Iampietro, D. J.; Brasher, L. L.; Kaler, E. W.; Stradner, A.; Glatter, O. *J. Phys. Chem. B* **1998**, *102*, 3105.
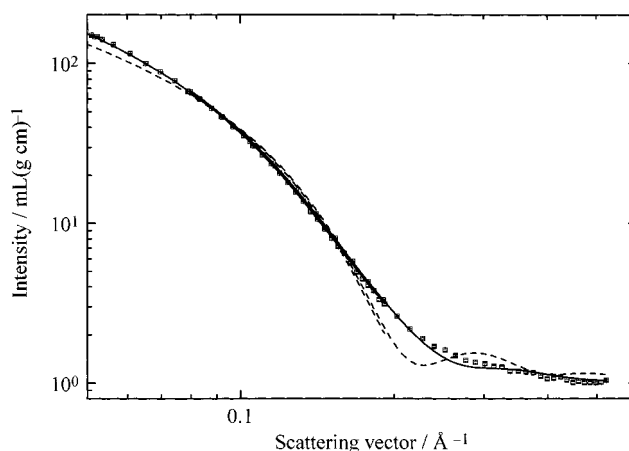(14) Bergström, M.; Pedersen, J. S. *Langmuir* **1998**, *14*, 3754.

formed in mixtures of the same surfactants (SDS and DTAB) at the same temperature, but using 0.1 M NaBr brine as solvent. The analyses have led us to modify the conclusions drawn in ref 14 concerning the details of the geometry of the mixed micelles formed in the absence of added salt. In contrast to what is generally believed, we find that the equilibrated micelles are shaped as rigid tablets or flexible ribbons. A more extensive and detailed presentation of our results will be given in a forthcoming paper.

Results and Discussion

The experiments were performed on the SANS instrument at the DR3 reactor, Risø National Laboratory.[15] The scattering data were analyzed by means of fitting them to various form factors for particles of different geometry using conventional least-squares methods.[16] The interactions between charged micelles were, when necessary, taken into account by means of the structure factor derived by Hayter and Penfold[17] from the Ornstein–Zernike equation and the rescaled mean spherical approximation. In their approach the soft repulsive potential between two macroions with an effective charge z_{eff} surrounded by a diffuse double layer of counter- and coions was calculated from the Poisson–Boltzmann theory. Further experimental details can be found in ref 14.

A summary of the various microstructures found in the two solvents is given in the ternary diagrams in Figure 1. The samples were equilibrated for about 24 h at 40 °C before measurement and have an overall surfactant concentration $c_{surf}^{tot} \equiv$ [SDS] + [DTAB] = 0.125–5.0 wt % (pure D$_2$O) and 0.025–1.0 wt % (brine) and an overall molar surfactant composition $X \equiv$ [SDS]/([SDS] + [DTAB]) = 0.15–0.40 and 0.60–0.85 (pure D$_2$O) and X = 0.10–0.35 and 0.65–0.90 (brine). A combination of a free monomer effect (see further below) and interactions between the comparatively voluminous vesicles caused a transition from either micelles or stacks of lamellar sheets to vesicles as c_{surf}^{tot} decreased for a given X. As the mixtures were further diluted, the vesicles grew in size and, eventually, a precipitate formed. The vesicles formed in pure water were clearly destabilized upon addition of NaBr.

The scattering data of the samples containing the largest micelles in brine show the typical q^{-1} behavior of a rodlike particle but could not at all be fitted assuming a strictly circular cross section (cf. Figure 2). Analyses of the data by model-independent inversion methods provide important information on the cross-section structure of the elongated micelles.[18–20] The analyses show that the maximum diameter is much larger than a fully extended surfactant molecule, and hence, the hypothesis of a polydisperse strictly circular cross section is completely unrealistic. Moreover, the radial cross-section scattering length density profile does not appear as a simple two-step function, as would be expected for a monodisperse circular symmetrical cross section consisting of an inner hydrocarbon part and an outer head group part. Reasonable fits for cylindrical micelles where either swollen end-caps or a two-shell model for the cross-section scattering length density were included into the models could only be obtained assuming unphysical values for the end-cap

(15) Pedersen, J. S. *J. Phys. IV (Paris) Colloq. C8* **1993**, *3*, 491.
(16) Pedersen, J. S. *Adv. Colloid Interface Sci.* **1997**, *70*, 171.
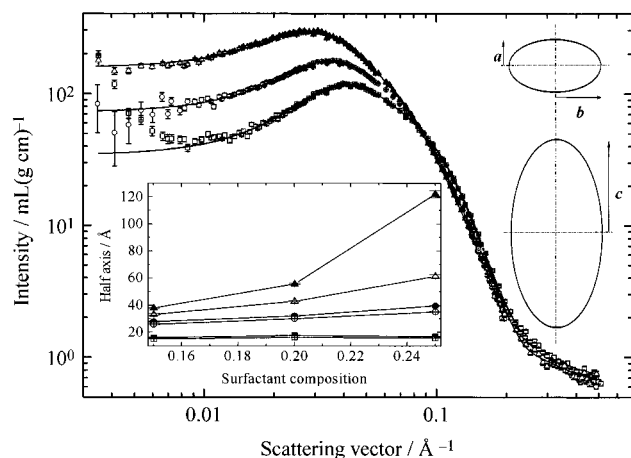(17) Hayter, J. B.; Penfold, J. *Mol. Phys.* **1981**, *42*, 409.
(18) Glatter, O. *J. Appl. Crystallogr.* **1977**, *10*, 415.
(19) Glatter, O. *J. Appl. Crystallogr.* **1980**, *13*, 577.
(20) Pedersen, J. S.; Schurtenberger, P. *J. Appl. Crystallogr.* **1996**, *29*, 646.

Figure 2. Normalized scattering intensity as a function of scattering vector q in the high-q range for [SDS]/[DTAB] = 80:20 and [SDS] + [DTAB] = 1.0 wt %. The solid lines represent the best available fit (0.05 < q < 0.6) assuming an elliptical cross-section resulting in the half-axes a = 13.4 Å and b = 26.7 Å. The dashed lines represent the best available fit (0.05 < q < 0.6) obtained assuming a circular cross-section giving a cylinder radius of 17.6 Å. The agreement of the former fit as measured by χ^2 equals 7.5, and for the latter, χ^2 = 207.

radius and the outer shell thickness and scattering length density, respectively.

Hence, the only models that could satisfactorily fit the data for all samples where micelles were found were ones for tablet-shaped micelles, that is, elongated bilayer fragments. These models also give the best fits, as measured by χ^2 (cf. ref 21) for all samples, including the ones containing small micelles in the absence of added salt. The agreement between data and models was very good, and thus, it was not necessary to include the polydispersity of the cross-section dimensions (thickness and width). For some of the samples polydispersity with respect to the micelle length and/or flexibility of the aggregates must be accounted for. The smallest micelles were best fitted with a model for triaxial ellipsoidal particles with half axes a < (related to the thickness) < b (related to the width) < c (related to the length). In the absence of added salt, we found half the thickness of the DTAB-rich micelles to be 16.0 ≤ a ≤ 18.1 Å whereas the SDS-rich micelles appeared to be somewhat thinner; i.e., 15.0 Å ≤ a ≤ 16.7 Å. The corresponding values for the case where 0.1 M NaBr was used as a solvent, and, hence, the counterions are located closer to the micelle surfaces, are 14.4 Å ≤ a ≤ 15.7 Å (DTAB-rich micelles) and 13.2 Å ≤ a ≤ 15.4 Å (SDS-rich micelles). Typical errors of a are ±0.2 Å. Hence, the thickness is, in general, substantially less than twice a fully stretched hydrocarbon chain, in accordance with a more favorable hydrocarbon chain conformational entropy.[22] The same effect also accounts for the trend, in the case of using brine as solvent, of decreasing bilayer thickness with increasing micelle size. There is however a counteracting influence, arising from the electrostatic contribution to the free energy of the micelles, tending to increase a as $X \rightarrow$ 0.5, which might be important for the micelles formed in pure D$_2$O, where the same trend of decreasing bilayer thickness with increasing micelle size is absent.

In both solvents there is a monotonic increase in width as well as the length of the micelles as the equimolar surfactant composition is approached at a given c_{surf}^{tot}. The

(21) Bevington, B. R. *Data Reduction and Error Analysis for Physical Sciences*; McGraw–Hill: New York, 1969.
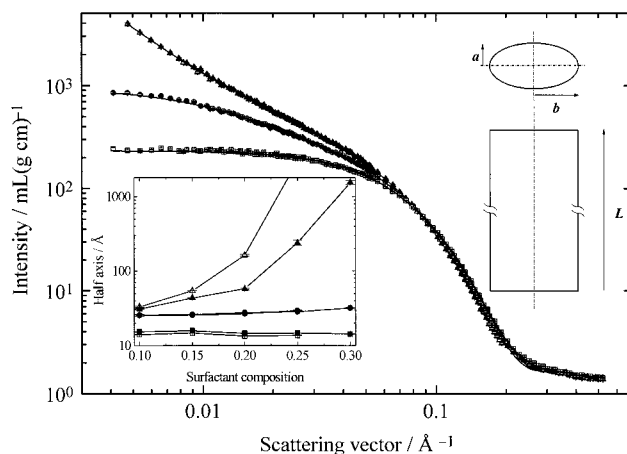(22) Gruen, D. W. R. *J. Phys. Chem.* **1985**, *89*, 153.

Figure 3. Normalized scattering intensity for [SDS]/[DTAB] = 85:15 (squares, bottom data), 80:20 (circles, middle data), and 75:25 (triangles, upper data) at an overall surfactant concentration of 1.0 wt % in the absence of added salt. The lines represent the results from fits with a model for monodisperse triaxial ellipsoids (right insert). The geometrical dimensions of the micelles at [SDS]/[DTAB] = 85:15 were found to be a = 15.0 Å, b = 25.7 Å, and c =33.0 Å. The effective charge divided by the charge of the fully dissociated micelle was z_{eff}/z_{ideal} = 0.18, and the agreement of the fits as measured by χ^2 was equal to 2.9. The corresponding values for the micelles at [SDS]/[DTAB] = 80:20 were a = 16.2 Å, b = 29.9 Å, c = 42.7 Å, z_{eff}/z_{ideal} = 0.18, and χ^2 = 5.3, and at [SDS]/[DTAB] = 75:25, a = 15.7 Å, b = 34.9 Å, c = 61.3 Å, z_{eff}/z_{ideal} = 0.22, and χ^2 = 2.2. The left inset shows the half axes related to the thickness a (squares), the width b (circles), and the length c (triangles), with error bars, plotted against the surfactant compositions $1 - X$ for SDS-rich micelles (open symbols) and X for DTAB-rich micelles (solid symbols) at an overall surfactant concentration of 1.0 wt % in the absence of added salt.

micelles formed in pure D_2O grow significantly in both directions as $X \rightarrow 0.5$ (cf. Figure 3). b increases from about 25 Å (X = 0.15 and 0.85) to 40 Å (X = 0.25−0.30) or 45 Å (X = 0.70), and c increases from about 35 Å (X = 0.15 and 0.85) to 110−140 Å (X = 0.30) and 140−160 Å (X = 0.70). Typical errors of b are ±0.5 Å. At about X = 0.30 and 0.70 there are abrupt transitions from comparatively small micelles to large lamellar sheets, which is theoretically expected for aggregates growing significantly in two dimensions.[14,23] Examples of scattering data, together with fits, for SDS-rich samples of various compositions, in the absence of added salt, at a given value of c_{surf}^{tot} = 1.0 wt % are shown in Figure 3.

In striking contrast to the case where no extra salt was added, the micelles in 0.1 M NaBr brine grow much stronger in length than in the width direction (cf. Figure 4). As a matter of fact, we observed SDS-rich ribbonlike micelles as long as several thousand angstroms at compositions (X = 0.75) near those where a lamellar phase is observed (cf. Figure 1b). Sufficiently elongated micelles appear to be significantly polydisperse in the length direction. Hence, we have fitted the data of these samples with a model for polydisperse rods with a (volume-weighted) average length $\langle L \rangle$ and an elliptical cross-section with half axes a (related to the thickness) and b (related to the width) (cf. Figure 4). The half axis b increases only slightly from about 25 Å at X = 0.10 and 0.90 to about 30 Å at X = 0.25−0.30 and 0.75. The lengths, however, of the micelles increase from about c = 35 Å (X = 0.10 and 0.90) to $\langle L \rangle \approx 3000$ Å at X = 0.30 while the SDS-rich micelles at X = 0.75 were so long (at least 5000 Å) that their size

(23) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525.

Figure 4. Normalized scattering intensity for [SDS]/[DTAB] = 85:15 (squares, bottom data), 80:20 (circles, middle data), and 75:25 (triangles, upper data) at an overall surfactant concentration of 1.0 wt % in a 0.1 M NaBr solution. The lines represent the results from fits with models for monodisperse triaxial ellipsoids (squares) (see inset in Figure 3), polydisperse rigid rods with elliptical cross sections (circles) (right inset), and self-avoiding wormlike ribbons with elliptical cross sections (triangles). The geometrical dimensions of the tablet-shaped micelles at [SDS]/[DTAB] = 85:15 were a = 14.7 Å, b = 25.6 Å, c =54.3 Å, and χ^2 = 4.3. The (volume-weighted) average length of the polydisperse ($\sigma_L/\langle L \rangle \approx 1$) rigid rods at [SDS]/[DTAB] = 80:20 was $\langle L \rangle$ = 327 Å, and the half axes of the elliptical cross section were a = 13.4 Å and b = 26.7 Å and χ^2 = 5.5. The half axes of the elliptical cross section of the ribbonlike micelles at [SDS]/[DTAB] = 75:25 were a = 13.7 Å and b = 29.5 Å, the persistence length l_p = 222 Å, and χ^2 = 5.5. The size and polydispersity of the ribbonlike micelles in the length direction cannot be resolved. The left inset shows the half axes related to the thickness a (squares), the width b (circles), and the 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 $1 - X$ for SDS-rich micelles (open symbols) and X for DTAB-rich micelles (solid symbols). For the polydisperse micelles formed at 20:80 ≤ [SDS]/[DTAB] ≤ 80:20, the (triangular) symbols represent half the volume-weighted average length $\langle L \rangle/2$.

distribution could not be determined from our SANS data. The relative standard deviation $\sigma_L/\langle L \rangle$, based on the volume-weighted length distribution, of the most polydisperse micelles was found to be slightly less than unity with comparatively large errors, and in the model fits of these samples $\sigma_L/\langle L \rangle$ was fixed to 0.95. As the micelles become sufficiently elongated, that is, $\langle L \rangle > 900$ Å, the data could only be fitted with a model for self-avoiding wormlike micelles[24] with elliptical cross sections. Examples of scattering data, together with fits, for SDS-rich samples of various compositions in 0.1 M NaBr brine at a given value of c_{surf}^{tot} = 1.0 wt % are shown in Figure 4.

For a given X, we found a clear trend of decreasing micelle size with increasing c_{surf}^{tot} for the case where brine was used as solvent, mostly pronounced in the length direction. For example, at X = 0.80, $\langle L \rangle$ decreases from 916 Å at c_{surf}^{tot} = 0.125 wt %, via 472 Å at c_{surf}^{tot} = 0.25 wt % and 439 Å at c_{surf}^{tot} = 0.50 wt %, to 327 Å at c_{surf}^{tot} = 1.0 wt %. The same trend can also be seen, but to a somewhat less extent, for micelles formed in the absence of added salt, the growth of which is significant with respect to both width and length. It is difficult to take any interparticle interference effects into account in our analysis of a collection of considerably polydisperse and anisotropic

(24) Pedersen, J. S.; Schurtenberger, P. *Macromolecules* **1996**, *29*, 7602.

particles at, for example, $X = 0.80$ in 0.1 M NaBr, and the neglect of them may influence the quantitative outcome of $\langle L \rangle$. An estimation of the contribution of the interparticle interference effects[25] to the scattering data indicates that the micelle size obtained in our model fit for $X = 0.80$ and $c_{\text{surf}}^{\text{tot}} = 1.0$ wt % differs with not more than roughly 15% from the real value and with even less for the samples at lower $c_{\text{surf}}^{\text{tot}}$. Hence, we can safely conclude that the general trend of a decreasing micelle size with increasing $c_{\text{surf}}^{\text{tot}}$ is not influenced by the neglect of interparticle interference effects in our model fits.

The effect can be rationalized considering the fact that a certain amount of the surfactants are located as free monomers in the surrounding bulk solution. It appears that the free monomer chemical potential (or, equivalently, the free monomer concentration) of the surfactant in excess is always much larger than the corresponding quantity for the surfactant in deficit. The large and unfavorable electrostatic work of bringing extra charge, that is, the surfactant in excess, compared with the canceling effect of bringing the surfactant in deficit to the micelle surface entails a ratio $c_{\text{excess}}^{\text{free}}/c_{\text{deficit}}^{\text{free}}$ as large as 10^5 to 10^7 (unpublished model calculations), depending on the composition of the aggregates. Thus, virtually all free monomers in the bulk solution are surfactants in excess, and hence, when a mixed surfactant solution is diluted at 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. As a result, following a dilution path for a given X, the micelles grow in size and, eventually, a transition to either vesicles or lamellar sheets occurs. The vesicles grow in size as their surface charge density decreases upon further dilution, and subsequently, a precipitate (DTA$^+$DS$^-$) is formed.

Moreover, when extra salt is added to the surfactant solutions, free monomers of the surfactant in excess are transferred into the aggregates and, consequently, increase the surface charge density of the aggregates. This, together with the fact that the work of bending a planar bilayer into a geometrically closed vesicle increases sharply with salt concentration,[26,27] accounts for the observed destabilization of vesicles and the formation of either micelles or lamellar sheets upon addition of NaBr to a solution of SDS/DTAB vesicles in pure D$_2$O (cf. Figure 1). The effect also accounts for the fact that the precipitate begins to form at lower surfactant concentrations upon addition of salt.

The persistence length was observed to increase from $l_{\text{p}} = 99$ Å at $X = 0.75$ and 0.25 wt % to $l_{\text{p}} = 208$ Å at $X = 0.80$ and 0.125 wt % as a result of an increasing surface charge density of the micelles. The same effect most probably also accounts for the increase of the persistence length with $c_{\text{surf}}^{\text{tot}}$ for $X = 0.75$ ($l_{\text{p}} = 222$ Å at 1.0 wt %) although the absence of interparticle interference effects in our data analyses may affect the quantitative outcome of the most concentrated samples measured.

Concluding Remarks

The discovery presented in the present paper that micelles formed in mixtures of an anionic and a cationic surfactant are shaped as rigid tablets or flexible ribbons is very important in order to understand ordinary surfactant systems, and as a matter of fact, it points toward a solution of the problem of structural change in dilute surfactant systems.

The growth of charged mixed micelles with decreasing surface charge density can be qualitatively understood as an effect of the decreasing importance of the entropy of mixing counterions associated with the surfactant aggregate with solvent. However, a more sophisticated thermodynamic analysis is required in order to account for the observed remarkably different kinds of growths with respect to width and length between tablet-shaped micelles formed in pure water and brine, respectively. It is our belief that such an analysis can be performed by means of considering a tablet-shaped micelle as consisting of three different geometrical parts: a central planar bilayer part surrounded by straight half cylindrical rims along the sides and two bent half toroids at the ends. The actual dimension of a tablet-shaped micelle, for a given solution state, is then determined by the free energies of forming the three geometrical parts of the micelle.

(25) Jerke, G.; Pedersen, J. S.; Egelhaaf, S. U.; Schurtenberger, P. *Phys. Rev. E* **1997**, *56*, 5772.

(26) Bergström, M.; Eriksson, J. C. *Langmuir* **1996**, *12*, 624.

(27) Bergström, M. *Langmuir* **1996**, *12*, 2454.