# Interaction of ABA Block Copolymers with Ionic Surfactants: Influence on Micellization and Gelation

## E. Hecht,<sup>†</sup> K. Mortensen,<sup>‡</sup> M. Gradzielski,<sup>§</sup> and H. Hoffmann<sup>\*,†</sup>

University of Bayreuth, Physical Chemistry I, 95440 Bayreuth, Germany, and Physics Department, Risoe National Laboratory, DK-4000 Roskilde, Denmark

Received: October 24, 1994<sup>®</sup>

Block copolymers of the poloxamer type  $EO_xPO_yEO_x$  (with EO = ethylene oxide and PO = propylene oxide) from micelles in aqueous solution that have a hydrophobic core of PO blocks and a strongly hydrated shell of EO blocks. The critical micellization temperature (cmt) of the poloxamers is strongly influenced by cosolutes such as surfactants. The interaction of F127 ( $EO_{97}PO_{69}EO_{97}$ ) with the anionic surfactant SDS was investigated by small-angle neutron scattering (SANS), static light scattering, and differential scanning calorimetry (DSC). It is found that addition of SDS can suppress the micellization of F127 completely. A simple model is proposed which describes the suppression of polymer micelles by ionic surfactant. The surfactant binds cooperatively on the block copolymer molecules, and the hydrophobic block is thereby made hydrophilic. At saturation conditions four to five SDS molecules bind to one F127 molecule. The bound amount of SDS increases somewhat with increasing polymer concentration. At higher concentration ( $w \ge 20$  wt %), pure F127 forms a cubic gel with increasing temperature. The gel region increases with increasing F127 concentration. Addition of SDS to a fixed F127 concentration decreases the gel region, until the gel completely disappears. The "melting" of the gel is a result of the suppression of the poloxamer micelles. With increasing surfactant concentration the hard sphere volume fraction  $\Phi$  decreases below 0.53, the critical value for hard sphere crystallization.

## 1. Introduction

Block copolymers of the type  $EO_xPO_yEO_x$  (with EO = ethylene oxide and PO = propylene oxide), also called poloxamers, have a wide industrial application and are commercially available under the trade names PLURONICS and SYNPER-ONICS. They behave in many ways like normal hydrocarbon surfactants. In aqueous solution they form micelles and lyotropic liquid crystalline phases.<sup>1-14</sup> Their surface activity depends strongly on temperature. Above the critical micellization temperature (cmt) or above the critical micellization concentration (cmc) they form micelles with a core containing the hydrophobic PO blocks and a shell of the hydrated EO blocks.

At higher concentrations the micelles form a liquid crystalline gel with a body-centered cubic structure.<sup>2,8-10,14</sup> This gel shows inverse temperature behavior; that is, with increasing temperature the aqueous solution is transformed into a stiff gel with a high yield stress value.<sup>2</sup> Further increase of temperature leads to a breakdown of the gel structure, again resulting in a solution with low viscosity.<sup>5,6</sup> The temperature range for the gel phase depends on the poloxamer concentration and increases with increasing concentration. The existence of the gel phase can be influenced by addition of the homopolymers PEO or PPO.<sup>15</sup> Addition of PEO results in a decreasing stability of the gel. With increasing PEO concentration the temperature range for the gel phase decreases and finally vanishes at a sufficiently high concentration. Low molecular weight PPO, on the other hand, increases the stability region of the gel, which is a consequence of the solubilization of the latter in the block copolymer micelles.

Salt also influences the gelation process.<sup>6,16,17</sup> Electrolytes such as KCl, NaCl, and KF shift the gel phase to lower temperatures, whereas addition of NaSCN results in a shift to higher temperatures. The same effect is obtained for the cloud point (CP) as a function of the electrolyte concentration.<sup>16,18</sup>

In their technical application poloxamers often are used in combination with ionic surfactants. Recent studies showed that ionic and even zwitterionic surfactants strongly interact with poloxamers.<sup>17-21</sup> Addition of low SDS concentration to L64 (EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>) increased its CP drastically due to formation of mixed aggregates with polyelectrolyte character.<sup>18</sup> With fluorescence quenching measurements it has been shown that addition of SDS to L64 and F68 (EO<sub>78</sub>PO<sub>30</sub>EO<sub>78</sub>) leads to the formation of mixed micelles.<sup>19</sup> With increasing SDS concentration the content of SDS in the mixed micelle increases, whereas the content of poloxamer decreases. At high surfactant concentration there are SDS aggregates left with one incorporated poloxamer molecule. In a recent paper we showed that addition of ionic and zwitterionic surfactants to F127 (EO<sub>97</sub>PO<sub>69</sub>EO<sub>97</sub>) suppresses the micelle formation of the block copolymer.<sup>20,21</sup> With increasing surfactant concentration the F127 micelles disappear in favor of mixed aggregates with intermediate size. At higher concentrations these particles also disappear in favor of aggregates with one F127 molecule and several surfactant molecules. Data from electric birefringence showed that these  $F127/SDS_x$  aggregates are nonspherical, but have a very short rotational relaxation time. Above the saturation of F127 with ionic surfactant the F127/SDS<sub>x</sub> aggregates grow to normal SDS micelles, which have one F127 molecule (i.e. its PO block) incorporated.

It can be expected that the presence of surfactants also influences the gel phase. Like ethanol and urea, addition of SDS to F88 ( $EO_{100}PO_{34}EO_{100}$ ) increases the gelation temperature.<sup>17</sup> The effect of SDS has been attributed to solubilization of SDS into F88 micelles, whereas ethanol and urea mainly act

© 1995 American Chemical Society

<sup>\*</sup> To whom correspondence should be addressed.

<sup>&</sup>lt;sup>+</sup> University of Bayreuth.

<sup>&</sup>lt;sup>‡</sup> Risoe National Laboratory

<sup>&</sup>lt;sup>§</sup> Present Address: Ecole Normale Superieure, Laboratoire de Physique Statistique, Paris Cedex 05, France.

<sup>&</sup>lt;sup>®</sup> Abstract published in Advance ACS Abstracts, March 1, 1995.

#### ABA Block Copolymers and Ionic Surfactants

as water structure breakers and hence disturb the poloxamer hydration sphere.

## 2. Experimental Section

**2.1.** Materials. Pluronic F127, MW = 12500 g/mol, 70 wt % EO (according to the manufacturer), was obtained from BASF/Wyandotte. By <sup>1</sup>H-NMR the EO content was determined to be 67 wt %. In GPC measurements a 0.6 wt % solution of F127 in DMF (30 °C) shows a single elution peak with a small shoulder at the low molecular weight side. This probably corresponds to a small contamination by diblock copolymer. SDS research grade obtained from Serva/Germany and NaCl p.a. obtained by Merck were used as received. D<sub>2</sub>O was supplied by Roth and contains 0.3% H<sub>2</sub>O. Solutions were made both in D<sub>2</sub>O and in twice distilled H<sub>2</sub>O to compare the influence of solvent on the aggregation properties of F127.

2.2. Small-Angle Neutron Scattering (SANS). Small-angle neutron scattering experiments were performed using the Risoe-SANS facility. Three spectrometer settings were applied to give good data over a wide range of momentum transfer q ( $q = 4\pi/\lambda \sin(\theta/2)$ ) given by the scattering angle  $\theta$  and the neutron wavelength  $\lambda$ ). Neutrons (3, 6, and 8 Å) were applied with sample-to-detector distances of respectively 3, 3, and 6 m. The neutron wavelength resolution was  $\Delta\lambda/\lambda = 0.18$ , the neutron beam collimation was determined by pinhole sizes of 16 and 7 mm in diameter at source and sample positions, respectively, and the collimation length was equal to the sample-to-detector distance. The smearing induced by the wavelength spread, the collimation, and the detector resolution was included in the data analysis discussed below, using Gaussian approximations for the different terms.<sup>22</sup>

The samples were mounted in sealed quartz containers (Suprasil from Hellma, FRG), with a 2 mm flight path. The scattering data were corrected for the background arising from the quartz cell with  $D_2O$  and from other sources, as measured with the neutron beam blocked by plastic containing boron at the sample position. The incoherent scattering from H<sub>2</sub>O was used to determine deviations from a uniform detector response and to convert the data into absolute units (cm<sup>-1</sup>).

The scattering patterns discussed in the present paper are all azimuthally isotropic. By azimuthally averaging, the data have been reduced to the one-dimensional I(q) scattering functions, which are only dependent on the absolute value of q.

**2.3. Differential Scanning Calorimetry (DSC).** Measurements were made with a Setaram Micro DSC in the temperature range between 0 and 100 °C. All poloxamers show an endothermic transition peak on heating and an exothermic peak on cooling. For the slow scanning rate of 0.2 K/min the two peaks are at the same temperature and show no kinetic retardation.  $T_{min}$  is the temperature in the peak minimum of the heating cycle. The cmt is defined as the temperature at the intersection of the tangent at the first inflection point of the peak with the base line.

2.4. Static Light Scattering. For all measurements a Chromatix KMX-6 photometer and a He/Ne laser were used to determine the Rayleigh ratio  $R_{\theta}$  at  $\theta = 6-7^{\circ}$ . From these values the scattered intensity of pure water was subtracted to get  $\Delta R_{\theta}$ . The solutions were filtered through a Schleicher & Schuell filter with 0.2  $\mu$ m pore size.

**2.5. Phase Diagram.** All solutions were prepared by weight and kept at 4  $^{\circ}$ C to dissolve all block copolymer. For higher SDS concentrations the solutions sometimes were heated to room temperature, to redissolve crystallized SDS. To scan the phase behavior of the F127/SDS mixtures, they were sealed in glass tubes and thermostated for at least 6 h at the corresponding temperature. At the phase boundary to the gel region this time



**Figure 1.** Light scattering of 1 wt % F127 + SDS/NaCl and 10 wt % F127 + SDS/NaCl at T = 25 °C. NaCl was added in equimolar amounts to SDS to avoid electrostatic repulsion. All solutions were made in H<sub>2</sub>O.

was prolonged up to several days. Between crossed polarizers the solutions were examined macroscopically and the tubes were inverted, to check the formation of the isotropic stiff gel. Above a certain temperature syneresis occurs; that is, a small drop of dilute solution separates from the gel. This syneresis is thermally reversible and occurs once more, when the gel is dissolved by cooling and is heated again. This phenomenon has also been found by Bedells et al.,<sup>23</sup> who investigated the gelling behavior of diblock copolymers of ethylene oxide and butylene oxide.

## 3. Results and Discussion

3.1. Micellization Process. Poloxamer solutions with high enough concentration show an endothermic transition on heating. In the same temperature range the light scattering of the solutions increases dramatically due to the formation of micelles.<sup>2,13</sup> The O-C-C-O segments in the PO block can be divided into a group with polar conformation and one with (almost) nonpolar character. At low temperature the polar conformation is preferred, and so the poloxamer is completely soluble in water. At higher temperature the statistical weight of the nonpolar conformation increases, and so the poloxamerpoloxamer interaction increases, whereas the poloxamer-water interaction decreases.<sup>6</sup> The DSC peak therefore is a result of dehydration of the PO blocks, which is caused by temperatureinduced conformational changes. Hence, the peak area can be described as the micellization enthalpy  $\Delta H_{mic}$ . The results show that  $\Delta H_{\rm mic}$  cannot be assigned to an exact temperature but to a temperature range of about 10 °C. The onset of the peak can be attributed to the critical micellization temperature (cmt). This cmt strongly depends on the concentration of the poloxamer and decreases linearly with increasing concentration.9,12,13,21

In H<sub>2</sub>O  $\Delta H_{\text{mic}}$  for F127 is 36.7 ± 1.4 J/g F127, corresponding to 460 ± 20 kJ/mol F127. Changing to the solvent D<sub>2</sub>O  $\Delta H_{\text{mic}}$  is, within experimental error, the same and the peak is shifted by 0.5-1 °C to lower temperatures.

As shown earlier<sup>20</sup> addition of SDS to a micellar solution of F127 leads to a drastic decrease of the light-scattering intensity (Figure 1). The decrease is the result of the binding of SDS onto F127, which results in a suppression of the F127 micelles. Increasing the SDS concentration will decrease the concentration of free F127 molecules. Therefore, the extent of aggregation of monomeric F127 to polymer micelles will be reduced by surfactant. At the saturation concentration of surfactant every F127 molecule will be involved in mixed aggregates.

This process can be seen in the DSC curves.<sup>20</sup> At very low surfactant concentrations the micellization peak of F127 is not



Figure 2. DSC of 3 wt % F127 + SDS in D<sub>2</sub>O: peak onset (cmt) and peak minimum ( $T_{min}$ ) as a function of added SDS concentration; scanning rate = 0.2 K/min.



**Figure 3.** Micellization enthalpy  $\Delta H_{mic}$  of F127 from DSC as a function of added SDS concentration: 1 wt % F127 + SDS and 5 wt % F127 + SDS in H<sub>2</sub>O; 3 wt % F127 + SDS in D<sub>2</sub>O (for comparison with SANS results).

influenced; hence, no binding occurs or this binding of surfactant to F127 is reversible. At intermediate surfactant concentrations the peak area decreases with increasing concentration. At the same time the peak is somewhat shifted to lower temperatures. Further increase of the surfactant concentration shifts the peak to higher temperatures, before it completely disappears. In Figure 2 the peak minimum,  $T_{min}$ , and the onset temperature, cmt, are shown as a function of SDS concentration. Plotting the micellization enthalpy,  $\Delta H_{\rm mic}$ , as a function of the SDS concentration gives Figure 3. An increase of the F127 concentration shifts the whole curve to higher SDS concentrations. The SDS concentration at which  $\Delta H_{\rm mic}$  starts to decrease is called  $c_1$ , and the SDS concentration at which  $\Delta H_{\rm mic}$  reaches 0 is called  $c_2$ . At  $c_1$ , SDS starts to adsorb onto F127, and at  $c_2$ , F127 is saturated with SDS. From the difference between  $c_1$ and  $c_2$  the bound amount of SDS may be estimated (Table 1). For 1-3 wt % F127 the F127/SDS aggregates at saturation conditions contain four to five SDS molecules per F127 molecule. With increasing F127 concentration the bound amount of SDS increases significantly.

In a previous paper<sup>20</sup> we found that binding of SDS to F127 is not influenced by the presence of equimolar amounts of

TABLE 1: Critical Adsorption Concentration  $c_1$  andSaturation Concentration  $c_2$  for the Binding of SDS to F127(Data from Figure 3)<sup>a</sup>

w(F127)/ wt %	solvent	$c_1/mM$	c₂/mM	n <sub>SDS</sub> / (mol SDS/mol F127)
1	H <sub>2</sub> O	0.6	4.0	4.3
3	$D_2O$	1.7	13	4.7
5	$H_2O$	3.1	45	11

<sup>*a*</sup> The bound amount of SDS per F127,  $n_{SDS}$ , is calculated from the difference between  $c_1$  and  $c_2$ .

electrolyte. The plots for the series 1 wt % F127 + SDS and 1 wt % F127 + SDS/NaCl are practically indistinguishable. With SANS we wanted to have a better insight into the structure of the mixed aggregates and determine whether there is really no influence of salt. The poloxamer/SDS aggregates have polyelectrolyte character<sup>18</sup> and should therefore show interaction with electrolytes.

At first we have a look at the series with 3 wt % F127 + SDS. Figure 4 shows the scattering pattern at different SDS concentrations. A solution of 3 wt % F127 shows a curve shape of noninteracting particles, like Wanka et al.<sup>2,13</sup> and Mortensen et al.<sup>8-12</sup> found for micellar poloxamer solutions. Addition of SDS decreases the scattering intensity I(q) for  $q \rightarrow 0$  and shifts the scattering maximum to higher scattering vectors q.

For SDS concentrations below 10 mM, the scattering curves at high q values (<0.05 Å<sup>-1</sup>) largely overlap, whereas in the lower q range they differ significantly. Above 20 mM SDS the whole scattering pattern is completely different, with  $q_{\text{max}}$ at much higher values. This corresponds to the scattering of proper SDS micelles, which now are formed at  $c > c_2$ . Interesting to note is that at q = 0.055 Å<sup>-1</sup> almost all curves show intersection at the same scattering intensity I(q).

From simple geometrical calculations we can get information about the mean distance and the aggregation number of the particles. For 3 wt % F127 the number density of monomerically dissolved block copolymer  $\hat{c}_0$  corresponds to  $1.45 \times 10^{18}$ F127 molecules per cm<sup>3</sup>. From the mean volume per F127 molecule we can derive the mean distance between two polymers to be 88 Å. In an F127/SDS mixture the mean particle distance *D* is approximately given by

$$D = 2\pi/q_{\rm max} \tag{1}$$



Figure 4. Radial-averaged SANS pattern of 3 wt % F127 + SDS in D<sub>2</sub>O at various SDS concentrations and  $T = 27.2 \pm 0.4$  °C.

TABLE 2: Mean Aggregation Number of F127 for 3 wt % F127 + SDS as a Function of the SDS Concentration, with  $q_{\text{max}}$  from Figure 4, the Particle Density  $\hat{c}$  According to Eqs 1 and 2, and  $N_{\text{F127}}$  from the Ratio  $\hat{c}_0/\hat{c}$ 

[SDS]/mM	$q_{ m max}$ /Å $^{-1}$	ĉ/10 <sup>16</sup> particles/cm <sup>3</sup>	N <sub>F127</sub>
0	0.017 31	2.09	69
0.1	0.017 39	2.12	68
0.2	0.017 39	2.12	68
0.3	0.017 39	2.12	68
0.6	0.017 31	2.09	69
1	0.018 85	2.70	54
2	0.020 48	3.46	42
3	0.022 63	4.67	31
6	0.027 01	7.94	18
10	0.030 97	12.0	12
20	0.043 09	32.3	4.5
50	0.059 91	86.7	1.7
100	0.068 08	127	1.1

Assuming that at SDS concentrations below 10 mM the scattering of SDS is negligible compared to that of F127, we can calculate the particle density in the solution to be

$$\hat{c} = D^{-3} \tag{2}$$

The ratio between  $\hat{c}_0$  and  $\hat{c}$  now gives an estimate for the mean aggregation number of the F127 micelles. In Table 2 the data are summarized. For a 3 wt % solution at 27 °C F127 forms micelles with the mean aggregation number  $N_{F127} = 69$ . This agrees well with light-scattering data from Wanka et al.,<sup>13</sup> who found N to be 37 and 67 for 25 and 30 °C, respectively. Below a concentration of 1 mM addition of SDS does not change  $N_{F127}$ , whereas above 1 mM SDS  $N_{F127}$  decreases continuously. At 100 mM SDS  $N_{F127}$  reaches the value for monomerically dissolved F127. In other words, F127 now is incorporated in normal SDS micelles, showing the scattering behavior of SDS.

Comparing these data with the results from DSC (Table 1 and Figure 3) shows that at  $c_1 \approx 1.7 \text{ mM } N_{\text{F127}}$  starts to decrease; hence the adsorption of SDS onto F127 begins. At  $c_2 \approx 13$ mM  $N_{\text{F127}}$  is still higher than 1, also indicated by  $\Delta H_{\text{mic}} > 0$  in Figure 3. Even at 50 mM SDS, where the micellization process of F127 is completely suppressed ( $\Delta H_{\text{mic}} = 0$ ),  $N_{\text{F127}}$  is higher than 1. In Figure 3  $\Delta H_{\text{mic}}$  reaches the half-height (1/2) $\Delta H^{\circ}_{\text{mic}}$ at about 5 mM SDS. At this point only half of the F127 molecules contribute to the micellization process, the others being bound to F127/SDS aggregates. This concentration corresponds to an aggregation number  $N_{\text{F127}}$  of 22, which is only one-third that of a normal F127 micelle. The SDS concentration when the  $N_{\text{F127}}$  reaches the value (1/2) $N^{\circ}_{\text{F127}}$  can be estimated from Table 2 to be 3 mM. Although this concentration difference is not very large, it is significant.

The structural properties of the poloxamer micellar suspension can be treated as a monodispersed system of hard sphere interacting spheres.<sup>8</sup> The scattering function can be written as the product of the single-particle form factor P(q) and the structure factor S(q), describing the interparticle interferences:

$$I(q) = \Delta \varrho^2 N V^2 P(q) S(q)$$
(3)

where  $\Delta \varrho^2$  is the contrast factor and N is the number density of scatterers of volume V. The form factor P(q) is dominated by the micellar core radius  $R_c$  and can be approximated to P(q) of a dense sphere:

$$P(q) = \left(\frac{3}{(qR_c)^3}(\sin(qR_c) - qR_c\cos(qR_c))\right)^2$$
(4)

The structure factor S(q) describes the arrangement of the micelles. Using the classical Ornstein-Zernike approximation for the spatial correlations, and the Percus-Yevick approximation to describe the direct correlation between two scattering objects<sup>24</sup> with a hard sphere nearest neighbor interaction potential, the structure factor can be written in the analytical form

$$S(q) = \frac{1}{1 + 24\phi G(2qR_{\rm hs},\phi)/(2qR_{\rm hs})}$$
(5)

where G is a trigonometric function of the hard sphere interaction radius  $R_{\rm hs}$  and the hard sphere volume fraction  $\Phi$ . Thus, by least squares residual fitting the experimental scattering function can be analyzed in terms of three parameters characterizing the micellar aggregates: the core radius  $R_{\rm c}$  dominating the form factor P(q) and the hard sphere interaction parameters  $R_{\rm hs}$  and  $\Phi$ .

Figure 5 shows  $R_c$  and  $R_{hs}$  as a function of the SDS concentration. At low SDS concentrations  $R_c$  remains constant and decreases above ca. 0.6 mM continuously with increasing concentration. Above 20 mM SDS  $R_c$  again reaches a plateau. These two concentrations agree reasonably well with  $c_1$  and  $c_2$  from Figure 3.  $R_{hs}$  behaves somewhat different. At low SDS concentrations  $R_{hs}$  shows a slight increase and then remains constant, until at 1 mM SDS it decreases drastically. Even above 50 mM  $R_{hs}$  does not reach a plateau region, as  $R_c$  does.

Now we add NaCl in equimolar amounts to SDS, to decrease electrostatic repulsion between the charged aggregates. If this



**Figure 5.** 3 wt % F127 + SDS (filled symbols) and 3 wt % F127 + SDS/NaCl (1:1) (open symbols): hard sphere radius  $R_{hs}$  and core radius  $R_c$  as a function of the SDS concentration,  $T = 27.2 \pm 0.4$  °C.

repulsion prevents the F127/SDS aggregates from micellization to F127 micelles, salt should influence the adsorption process of SDS to F127. Figure 6 shows the SANS pattern for the system 3 wt % F128 + SDS/NaCl (1:1). Again the particle density  $\hat{c}$  and the mean aggregation number  $N_{\rm F127}$  can be calculated from  $q_{\rm max}$  (Table 3). In the presence of equimolar amounts of NaCl  $N_{\rm F127}$  starts to decrease already below 0.6 mM SDS. With increasing SDS concentration  $N_{\rm F127}$  decreases strongly, but even at 100 mM SDS it is slightly above 1; that is, F127 is not yet monomerically dissolved.

From fitting the scattering curves we obtain the micellar dimensions  $R_{hs}$  and  $R_c$  (Figure 5), which are compared to the data without NaCl. Up to 1 mM SDS the hard sphere radius  $R_{hs}$  remains constant and decreases rapidly when the SDS concentration is increased. As for the series without added NaCl,  $R_{hs}$  does not reach a plateau region, even at 100 mM SDS. The core radius  $R_c$  shows a slight decrease for low SDS concentrations and above 20 mM SDS, a plateau.

Comparing the series 3 wt % F127 + SDS and 3 wt % F127 + SDS/NaCl shows that the values for  $R_c$  are essentially the same, independent of the presence of NaCl. This means, that the mean aggregation number of the F127 micelles decreases with surfactant concentration. This decrease is rather weak, especially at low SDS concentrations. Therefore, the suppression of the F127 micelles by SDS is a continuous process without marked onset and saturation. This is confirmed by the DSC results in Figure 3. Already at concentrations below  $c_1$  $\Delta H_{mic}$  starts to decrease. This is due to the distribution of molar masses and even the block sizes. In a poloxamer solution we have molecules with different hydrophobic character. If we add surfactant, this will interact at first with the most hydrophobic species of poloxamer. At higher surfactant concentrations the critical aggregation concentration for less hydrophobic poloxamers will be exceeded, until all block copolymer molecules are saturated with SDS. Therefore, we cannot expect welldefined concentrations for  $c_1$  and  $c_2$ .

For  $R_{\rm hs}$  there is a small difference for the series 3 wt % F127 + SDS and 3 wt % F127 + SDS/NaCl. In the presence of NaCl  $R_{\rm hs}$  starts to decrease at lower SDS concentrations than without NaCl. Up to 20 mM, where the two curves again coincide,  $R_{\rm hs}$  for 3 wt % F127 + SDS/NaCl is smaller than that for 3 wt % F127 + SDS. Because in this concentration range the core radius is the same for both series, the difference in  $R_{\rm hs}$  is caused by contraction of the PEO shell. As has been shown,<sup>25.26</sup> NaCl decreases the cloud point of aqueous PEO solutions. This results from a collapse of the polymer coil, which now has a smaller dimension. At higher salt concentra-

tion this leads to a phase separation into a concentrated and a dilute polymer solution, i.e. clouding. In the case of poloxamers the micellar shell contains highly swollen PEO blocks and has a brushlike structure. With addition of small amounts of NaCl the thickness of the PEO brush is decreased due to this collapse. Therefore,  $R_{\rm hs}$  decreases, whereas  $R_{\rm c}$  remains constant.

Model for the Interaction between Poloxamer and Ionic Surfactant. Anionic, cationic, and even zwitterionic surfactants interact with the block copolymers and thereby suppress their micellization.<sup>20,21</sup> With increasing surfactant concentration the mean particle size in the mixture decreases. This can be achieved by different ways, which are shown schematically in Figure 7. At temperatures much lower than the cmt of the corresponding poloxamer concentration, the block copolymer molecules are all in the monomeric state P. Their hydrophobic character increases with increasing temperature and so does their surface activity.<sup>13</sup> At temperatures just below the cmt they show hydrophobic interaction with surfactant molecules in the solution. Thus, the aggregate  $PS_x$  is formed. Increasing the temperature above the cmt leads to micellization of the remaining poloxamer monomers P to  $P_n$ . This transition results in the micellization enthalpy  $\Delta H_{\rm mic}$ . The lower the concentration of free monomers P, the lower will be the overall micellization enthalpy of the solution. In fact, the area of the DSC peak decreases with increasing surfactant concentration. Due to the headgroup charge of the surfactants and the screening of the hydrophobic parts of the polymer, these aggregates now are highly hydrophilic. Hence, there is no motivation to form polymer micelles.

While the above reasoning corresponds to a DSC experiment, we examine now the light-scattering experiment. We assume that the temperature is above the cmt, and therefore the equilibrium between P and P<sub>n</sub> lies at the side of P<sub>n</sub>. The concentration of P is thus very low, as has been shown by lightscattering measurements. The cmc for the present conditions (F127 at 25 °C) is  $4 \times 10^{-3}$  wt %;<sup>2</sup> hence the concentration of P is negligible. Adding surfactant to a micellar poloxamer solution results in a decrease of the mean particle size. This can be achieved either by formation of smaller aggregates ( $P_aS_b$ ) or by a mixture of small  $(PS_x)$  and big  $(P_n)$  aggregates. In the latter case some polymer micelles  $P_n$  have to be dissolved to monomeric P, which then bind surfactant S to form  $PS_x$ . The average particle size now depends on the concentration ratio  $P_n/PS_x$ , which decreases with increasing surfactant concentration. In this manner a continuous decrease of the average particle size can be imagined, even though two discrete species of constant size are involved.

In the case of intermediate aggregates  $P_aS_b$ , three kinds of species should be detectable. Indeed this has been found for 1 wt % F127 + SDS/NaCl (1:1). Dynamic light scattering gave evidence for three species in equilibrium, corresponding to  $P_n$ ,  $P_aS_b$ , and  $PS_x$ .<sup>20</sup> For higher F127 concentrations, however, only two species were detectable, which correspond to  $P_n$  and  $PS_x$ . For higher surfactant concentrations there are only  $PS_x$  aggregates left. They grow to normal surfactant micelles, which have one poloxamer molecule incorporated. Above the cmc for the block copolymer/surfactant system there also occur micelles of pure surfactant,  $S_x$ .

**3.2. Gelation Process.** With high enough molecular weight and EO content, poloxamers can form stiff gels. At an effective volume fraction of  $\Phi = 0.53$  the polymer micelles form a liquid crystalline cubic structure.<sup>8-12</sup> This critical volume fraction can be obtained either by increasing the weight concentration (at constant temperature) or by increasing the temperature (at sufficiently high poloxamer concentration). At even higher temperatures the gel again melts to an isotropic solution with



Figure 6. Radial-averaged SANS pattern of 3 wt % F127 + SDS/NaCl (1:1) in D<sub>2</sub>O at various SDS concentrations and  $T = 26.3 \pm 0.8$  °C.



**Figure 7.** Possible mechanism for the destruction of poloxamer (P) micelles by surfactant (S) with n > a and m/n < b/a < x. At high surfactant concentrations also pure  $S_x$  micelles are formed, but for clarity they are not included in the scheme.

TABLE 3: Mean Aggregation Number of F127 for 3 wt % F127 + SDS/NaCl (1:1) as a Function of the SDS Concentration, with  $q_{max}$  from Figure 6, the Particle Density  $\hat{c}$  According to Eqs 1 and 2, and  $N_{F127}$  from the Ratio  $\hat{c}_0/\hat{c}$ 

[SDS]/mM	$q_{ m max}$ /Å $^{-1}$	ĉ/10 <sup>16</sup> particles/cm <sup>3</sup>	N <sub>F127</sub>
0	0.017 31	2.09	69
0.1	0.017 39	2.12	68
0.2	0.017 33	2.10	69
0.3	0.017 26	2.07	70
0.6	0.017 94	2.33	62
1	0.018 89	2.72	53
2	0.020 52	3.48	42
3	0.022 23	4.43	33
6	0.027 92	4.85	30
10	0.026 36	7.38	20
20	0.042 70	31.4	4.6
50	0.055 58	69.2	2.1
100	0.060 30	88.4	1.6

low viscosity. The temperature range of the gel phase depends on the poloxamer concentration. It increases with increasing block copolymer concentration.

As mentioned above, this gelation process can be influenced by additives. As shown by Malmsten and Lindman,<sup>15</sup> addition of PEO decreases the gel region of F127, until it vanishes at sufficiently high PEO concentration. This effect strongly depends on the molecular weight of the homopolymer. PEO 400 and PEO 600 hardly effect the gelation of F127, whereas PEO 6.000 increases the gelation temperature and simultaneously decreases the melting temperature. With higher MW of PEO the decrease of the gel region is more pronounced, whereas PEO 200.000 induces phase separation, rather than gel melting. PPO on the other side increases the gel region. PPO 400 does not influence the gelation temperature, because at this temperature PPO is infinitely soluble in water. At higher temperatures, however, PPO is solubilized in the micellar core due to lower solubility in water. With increasing PPO concentration the micellar dimensions increase and so does the melting temperature of the gel. PPO 4.000 on the other hand is too large to be solubilized. Hence 1 wt % PPO 4.000 cannot be solubilized by even 20 wt % F127.

Malmsten and Lindman also investigated the influence of a cationic polyelectrolyte on the gelation behavior of F127.<sup>15</sup> PDADMAC with a molecular weight of  $2 \times 10^6$  decreases the melting temperature with increasing concentration, whereas the gelation temperature remains constant. At the same time the cloud point of F127 decreases by increasing the polyelectrolyte concentration. Above a certain concentration the gel phase of F127 has completely vanished.

Vadnere et al.<sup>17</sup> investigated the influence of electrolytes on different poloxamer gels. Salts like NaCl, KCl, and Na<sub>2</sub>SO<sub>4</sub> decrease the gelation temperature with increasing concentration. This has been confirmed by Malmsten and Lindman.<sup>6</sup> They found that 1 M NaCl shifts the gelation temperature of F127 about 28 °C to lower temperatures. Both for the melting temperature and the cloud point, addition of NaCl leads to a decrease of 44 °C/M. The corresponding slope for the cmt of F127 was found to be 12 °C/M.<sup>21</sup> NaSCN as a typical "saltingin" cosolute, however, shifts the gel region to higher temperatures.<sup>6</sup>

Urea, ethanol, and SDS increase the gelation temperature.<sup>17</sup> For urea and ethanol this is probably due to the fact that they are water structure breakers. This disturbs the ordered hydration sphere around the PO block and hence increases the entropy in the polymer solution. The reason for the behavior of SDS, however, is still unknown, although Vadnere et al.<sup>17</sup> had assumed solubilization of SDS into poloxamer micelles.

In the following we investigate the influence of SDS on the gelling behavior of F127. Figure 8 represents a cut through the ternary phase diagram for F127/SDS/H<sub>2</sub>O at a fixed F127 concentration of 25 wt %. At this concentration the onset of gelation occurs at 16.0 °C. After passing a two-phase region at 18.5 °C we have an isotropic stiff gel, which is stable up to 70.0 °C. After passing the two-phase region we are in an isotropic phase with low viscosity. Further increase of the temperature leads to the formation of a system which shows shear-induced birefringence. The originally isotropic bluish solution shows birefringence upon shaking and becomes isotropic again upon standing. Addition of SDS results in an increase of the gelation temperature, whereas the melting



Figure 8. Phase diagram for 25 wt % F127 + SDS in H<sub>2</sub>O: circles, temperature at which syneresis occurs (a drop of dilute solution is expelled from the gel phase); SIB, shear-induced birefringence.



**Figure 9.** Phase diagram for 30 wt % F127 + SDS in H<sub>2</sub>O: circles, syneresis; SIB, shear-induced birefringence; N<sub>c</sub>, nematic rods.

temperature of the gel remains constant. At 110 mM SDS the gel region has completely disappeared in favor of an isotropic solution. Its viscosity decreases with a further increase of the surfactant concentration. At higher SDS concentration and low temperature SDS starts to crystallize, whereas at high temperature the single phase with flow birefringence is transformed into a three-phase region, with one solid and two liquid phases: one of them is isotropic and the other birefringent. The analogous phase diagram for 20 wt % F127 shows the same shape, but with a smaller gel region. Additionally, up to 100 °C there is no three-phase region. For 30 wt % F127 the gel region is more pronounced than for 25 wt % (Figure 9). Between the flow birefringent phase and the three-phase region as the upper limit and the gel phase as the lower limit a phase with permanent birefringence occurs. From micrographs with crossed polarizers the phase seems to be a nematic N<sub>C</sub> phase



Figure 10. Gel regions of the phase diagrams for  $F127/SDS/H_2O$  at fixed F127 concentrations. Only the one-phase regions are plotted.

(results not shown). It shows the same texture as was found for double-chain cationic surfactants.<sup>27,28</sup> The formation of nematic discs can be excluded, because the birefringence is independent of time and does not show formation of "pseudoisotropic" domains.

Mortensen et al.<sup>11,12</sup> found for poloxamers a transition from spherical to prolate micelles. For P85 (EO<sub>27</sub>PO<sub>39</sub>EO<sub>27</sub>), F87 (EO<sub>67</sub>PO<sub>39</sub>EO<sub>67</sub>), and F88 (EO<sub>96</sub>PO<sub>39</sub>EO<sub>96</sub>) this transition occurs in the temperature region of 60, 70, and 90 °C, respectively. In a recent study Schillén et al.<sup>29</sup> found evidence for rodlike micelles of P85 with a axis ratio of about 7. For high enough concentrations (15–25 wt % at 75 °C) these rods show flow birefringence, and at 30 wt % (75 °C) they finally form a hexagonal phase. The formation of rodlike micelles at high concentration would explain the observed flow birefringence, which relaxes immediately after the flow has stopped. When the rods are long enough, they become orientationally ordered, whereas their positions are still disordered. This may be the reason for the formation of the nematic phase, but more investigations have to be done here.

In Figure 10 the gel regions as a function of SDS concentration have been summarized. The amount of SDS which is needed to suppress the gelation (even in the two-phase region i + gel) increases with increasing F127 concentration. For 20, 25, and 30 wt % F127 these saturation concentrations are 70, 110, and 165 mM SDS, respectively. Assuming that all SDS is bound to F127, we can calculate the amount of bound surfactant per polymer molecule. For 20, 25, and 30 wt % F127 these values are 4.4, 5.5, and 6.9 mol SDS per mol F127. They lie in the same range as the results in Table 1, which were derived by suppression of the micellization of F127.

To have better insight into the suppression of the gel phase by addition of surfactant, we made SANS measurements. At a fixed F127 concentration of 25 wt % and a temperature of 23 °C we increased the SDS concentration, corresponding to a horizontal cut of the phase diagram in Figure 8. Figure 11 shows the scattering pattern for this series. From fitting these data we get  $R_c$  and  $R_{hs}$  as plotted in Figure 12. Both  $R_c$  and  $R_{hs}$ show a continuous decrease upon increasing SDS concentration. Even at 200 mM SDS there is no plateau region reached, suggesting that F127 is not yet saturated by SDS. From geometrical calculations it has been found that the aggregates at 200 mM SDS have to contain more than one F127 molecule. Hence, the suppression of the gel phase and the saturation of the F127 molecules are different processes. This can be easily seen from Figure 13. As has been shown by Mortensen,8-12gelation occurs when the volume fraction of hard spheres reaches 0.53. For SDS concentrations up to 80 mM  $\Phi$  remains constant at this value. The corresponding mixtures indeed form



Figure 11. Radial-averaged SANS pattern of 25 wt % F127 + SDS in D<sub>2</sub>O at various SDS concentrations and  $T = 23.2 \pm 0.6$  °C.



**Figure 12.** 25 wt % F127 + SDS: hard sphere radius  $R_{\rm hs}$  and core radius  $R_{\rm c}$  as a function of the SDS concentration,  $T = 23.2 \pm 0.6$  °C.



**Figure 13.** 25 wt % F127 + SDS in D<sub>2</sub>O: hard sphere volume fraction  $\Phi$  as a function of the SDS concentration,  $T = 23.2 \pm 0.6$  °C.

stiff gels. At higher SDS concentration  $\Phi$  gradually decreases; that is, the crystal structure of the gel melts. This melting can also be seen in Figure 8, where we leave the two-phase region i + gel in the direction of the isotropic solution. Interestingly, $in the region between 0 and 80 mM SDS <math>R_c$  and  $R_{hs}$  are decreasing, although  $\Phi$  is constant. This leads to the conclusion that the aggregation number of the aggregates decrease, and therefore so does their volume. At the same time, there are new aggregates formed with lower size but higher number density, so that the overall volume fraction of all hard spheres is still the same. Above 80 mM SDS the contribution of the big F127 micelles to  $\Phi$  is getting significantly lower and cannot be compensated by the contribution of the small aggregates. Hence,  $\Phi$  decreases below 0.53 and the gel melts.

Now we keep the composition of the mixture constant at 25 wt % F127 + 100 mM SDS and increase the temperature. This corresponds to a vertical cut of the phase diagram in Figure 8. At 24.5 °C the solution is still liquid, but has a high viscosity. With increasing temperature the viscosity increases, until above ca. 32 °C the gel is formed. For the same temperature scan the correlation peak in Figure 14 is getting more pronounced, as the temperature increases. The fitted values for  $R_c$  and  $R_{hs}$  are plotted in Figure 15. Both R<sub>c</sub> and R<sub>hs</sub> increase continuously with increasing temperature. The hard sphere volume fraction  $\Phi$  of this F127/SDS mixture as a function of temperature (Figure 16) shows the same behavior as pure poloxamers, when their concentration is increased.<sup>11</sup> Increasing the temperature for the former case and increasing the concentration in the latter case lead to an increase of  $\Phi$ , until the hard spheres crystallize (i.e. the gel forms) and  $\Phi$  becomes constant. In other words, when  $\Phi$  is constant, but  $R_c$  and  $R_{hs}$  are still increasing, smaller aggregates have to dissolve in favor of bigger micelles.

#### 4. Conclusions

1. The micelle formation of poloxamers is strongly influenced by additives such as surfactants. Anionic, cationic, and even zwitterionic surfactants interact with the block copolymers and thereby suppress their micellization. To describe this behavior, we developed a simple model and compared it with the experimental results. Depending on the surfactant concentration, different species are in equilibrium. With increasing concentration of surfactants the bigger aggregates vanish in favor of smaller ones. Above the saturation concentration only aggregates with one poloxamer molecule and several surfactant molecules exist.

2. The gel formation of poloxamers also is strongly influenced by surfactants. With increasing poloxamer concentration the gel region increases. At fixed poloxamer concentra-



Figure 14. Radial-averaged SANS pattern of 25 wt % F127 + 100 mM SDS in D<sub>2</sub>O at different temperatures.



**Figure 15.** 25 wt % F127 + 100 mM SDS in D<sub>2</sub>O: hard sphere radius  $R_{\rm hs}$  and core radius  $R_{\rm c}$  as a function of temperature.



Figure 16. 25 wt % F127 + SDS in  $D_2O$ : hard sphere volume fraction  $\Phi$  as a function of temperature.

tion the gel region decreases with increasing surfactant concentration, until the gel completely vanishes. This is a result of the destruction of polymer micelles by adsorption of surfactants. Thus, the hard sphere volume fraction  $\Phi$  decreases below 0.53, which causes the gel to melt.

Acknowledgment. Christine Thunig is gratefully acknowledged for helpful discussions dealing with the phase diagrams. This work was supported by the DFG (SFB 213) and the Fonds der Chemischen Industrie.

#### **References and Notes**

(1) Zhou, Z.; Chu, B. J. Colloid Interface Sci. 1988, 126, 171.

(2) Wanka, G.; Hoffmann, H.; Ulbricht, W. Colloid Polym. Sci. 1990, 268, 101.

(3) Brown, W.; Schillén, K.; Almgren, M.; Hvidt, S.; Bahadur, P. J. Phys. Chem. 1991, 95, 1850.

(4) Almgren, M.; Bahadur, P.; Jansson, M.; Li, P.; Brown, W.; Bahadur, A. J. Colloid Interface Sci. 1992, 151, 157.

- (5) Brown, W.; Schillén, K.; Hvidt, S. J. Phys. Chem. 1992, 96, 6038.
  (6) Malmsten, M.; Lindman, B. Macromolecules 1992, 25, 5440.
- (7) Yu, G.; Deng, Y.; Dalton, S.; Wang, Q.-G.; Attwood, D.; Price, C.; Booth, C. J. Chem. Soc., Faraday Trans. 1992, 88, 2537.
- (8) Mortensen, K.; Brown, W.; Nordén, B. Phys. Rev. Lett. 1992, 68, 2340.
  - (9) Mortensen, K. Europhys. Lett. 1992, 19, 599.
  - (10) Mortensen, K. Prog. Colloid Polym. Sci. 1993, 93, 72.
  - (11) Mortensen, K.; Brown, W. Macromolecules 1993, 26, 4128.
  - (12) Mortensen, K.; Pedersen, J. S. Macromolecules 1993, 26, 805.
- (13) Wanka, G.; Hoffmann, H.; Ulbricht, W. Macromolecules 1994, 27, 4145.
  - (14) Schmolka, I. R. J. Am. Oil Chem. Soc. 1991, 68, 206.
  - (15) Malmsten, M.; Lindman, B. Macromolecules 1993, 26, 1282.
- (16) Bahadur, P.; Pandya, K.; Almgren, M.; Li, P.; Stilbs, P. Colloid Polym. Sci. 1993, 271, 657.
- (17) Vadnere, M.; Amidon, G.; Lindenbaum, S.; Haslam, J. L. Int. J. Pharm. 1984, 22, 207.
- (18) Pandya, K.; Lad, K.; Bahadur, P. J. Macromol. Sci.-Pure Appl. Chem. 1993, A30, 1.

(19) Almgren, M.; van Stam, J.; Lindblad, C.; Li, P.; Stilbs, P.; Bahadur, P. J. Phys. Chem. 1991, 95, 5677.

- (20) Hecht, E., Hoffmann H. Langmuir 1994, 10, 86.
- (21) Hecht, E.; Hoffmann, H. Colloids Surf., in press.

(22) Pedersen, J. S.; Posselt, D.; Mortensen, K. J. Appl. Crystallogr. 1990, 23, 321.

- (23) Bedells, A. D.; Arafeh, R. M.; Yang, Z.; Attwood, D.; Padget, J. C.; Price, C.; Booth, C. J. Chem. Soc., Faraday Trans. **1993**, *89*, 1243.
- (24) Percus, J. K.; Yevick, G. J. Phys. Rev. **1958**, 110, 1.

(25) Florin, E.; Kjellander, R.; Eriksson, J. C. J. Chem. Soc., Faraday Trans. 1 1984, 80, 2889.

- (26) Ataman, M. Colloid Polym. Sci. 1987, 265, 19.
- (27) Hertel, G. Thesis, University of Bayreuth, 1989.
- (28) Hertel, G.; Hoffmann, H. Prog. Colloid Polym. Sci. 1988, 76, 123.
- (29) Schillén, K.; Brown, W.; Johnsen, R. M. Macromolecules 1994, 27, 4825.
- JP9428101