# Interactions between Methyl Cellulose and Sodium Dodecyl Sulfate in Aqueous Solution Studied by Single Molecule Fluorescence Correlation Spectroscopy

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ABSTRACT: The interactions between the anionic surfactant sodium dodecyl sulfate (SDS) and a hydrophobically modified nonionic polymer, methyl cellulose (MC), have been investigated in aqueous solution by fluorescence correlation spectroscopy (FCS) and rheology. FCS is used to follow the dynamics of different populations of single aggregates. We are able to follow the solution properties over a wide concentration range of both polymer and surfactant. At constant MC concentration the diffusion time of single aggregates increases gradually up to a certain SDS concentration and decreases to a minimum when the SDS concentration is further increased. This behavior coincides with the behavior of the zero shear viscosity. A model is proposed to explain the effect of surfactant concentration on polymer conformation and aggregation size.

## Introduction

The association between polymers and surfactants has drawn much attention throughout the past decades. Water-soluble polymer/surfactant systems are important for a variety of industrial applications in the areas of cosmetics, personal care, food, pharmaceutics, detergents, and mineral processing.[1,2] In particular, complexes between nonionic cellulose ethers and ionic surfactants in aqueous solution were investigated in the past.[3−16] Among the various nonionic cellulose ethers, methyl cellulose (MC) is the simplest and most well-known. Commercial MC is a heterogeneous polymer consisting of highly substituted hydrophobic zones and less substituted hydrophilic zones, resulting in an amphiphilic multiblock copolymer.[17] The amphiphilic nature of the polymer leads to weak inter- and intramolecular hydrophobic interactions in aqueous environment. The addition of an anionic surfactant is expected to lead to aggregation in the hydrophobic zones of MC. Earlier studies on polymer−surfactant systems have dealt with the adsorption of sodium dodecyl sulfate (SDS) on MC, poly(vinyl alcohol) and vinyl alcohol−acetate copolymers in aqueous solution using viscosity measurements and equilibrium dialysis.[18,19] Later studies on MC/SDS interactions include pressure-jump experiments[20] and steady-state fluorescence probe techniques[21] aiming to investigate the micellar stability and the microviscosity. Thermodynamic aspects have been studied in detail by Sing et al. for SDS and nonionic cellulose ethers having different hydrophobicity.[12] Kundu et al.[22] have studied the effect of salts and surfactant on the gelation of extremely dilute solutions of methyl cellulose.

Most of the above studies were carried out with conventional techniques accessing *macroscopic* solution properties. In addition, pulsed field gradient spin echo (PFG-SE) NMR measurements are also used to follow the formation of such complexes.[14−16,23−26] Fluorescence methods have been used over the past few decades to study polymer dynamics and polymer−surfactant systems with fluorescently labeled polymers.[27−29] In recent years single molecule fluorescence correlation spectroscopy has become very popular to investigate *microscopic* details of diffusion processes and complex formation in macromolecular solutions. Despite their indisputable potential, however, the technique was applied almost exclusively to biological systems in the past. First applications in the field of synthetic polymers have very recently been reported.[30−41]

In the present work, we demonstrate that the motion of individual SDS micelles and single MC/SDS aggregates can be followed by means of a single molecule fluorescence experiment, i.e., fluorescence correlation spectroscopy (FCS).[42,43] FCS monitors the motion of single dye molecules from observations of spontaneous intensity fluctuations of the fluorescence light when the molecule undergoes Brownian motion.[44] It thereby yields the mean diffusion time of the dye when passing through the illumination volume of a highly focused laser beam. To study complex formation with FCS, typically one of the partners is covalently labeled with a suitable dye.[45] Since the labeling procedure is often tedious, FCS has not become very popular for the study of synthetic polymers. Recently, however, it was shown that covalent labeling is not necessarily needed to study molecular aggregation by FCS. Zettl et al. studied various well-known surfactant systems and found that dyes with suitable polarity will spontaneously aggregate with surfactant micelles allowing to precisely follow the aggregation of the surfactant molecules.[46] It turned out that the choice of the proper polarity of the dye molecule is important if covalent labeling is to be avoided. In short: cationic dyes are needed to study anionic surfactants and vice versa.

The present work extends Zettl's approach to macromolecular complexes. As a model system we investigate complex formation between methyl cellulose and SDS at room temperature in water. We observe a characteristic slowing down of the dye molecules within a narrow window of SDS concentration, which is related to the formation and eventually the dissolution of MC/SDS complexes. The diffusion behavior of the complexes is compared to the zero shear viscosity obtained from rheological measurements. On the basis of the experimental results, we propose a model to explain the effect of surfactant concentration on polymer conformation and aggregation size.

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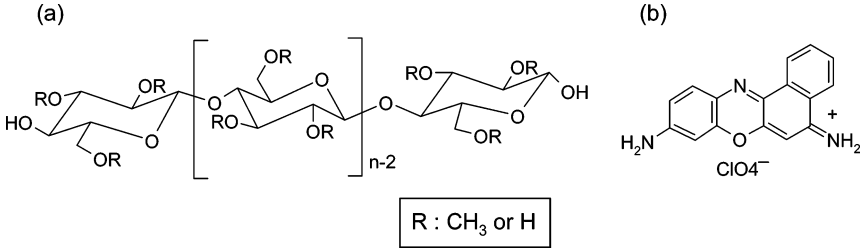


**Figure 1.** (a) Methyl cellulose. (b) Cresyl violet perchlorate.

## Experimental Section

**Materials.** Methyl cellulose (Figure 1a) purchased from Sigma Aldrich, Germany, was purified by dialysis. The manufacturer's specifications indicate that the viscosity of a 2 wt % solution was 4.0 Pa•s at 20 °C and that the methoxyl content and the degree of substitution are 27.5−31.5 wt % and 1.6−1.9, respectively. The weight-average molecular weight ($M_w$) is 313 800 g/mol as determined by static light scattering. Approximately 2 wt % of MC solution was prepared in Milli-Q water and allowed to stir for 2 days to get a homogeneous solution. The standard procedure for preparing stock solutions is reported elsewhere.[47] This solution was in a Spectra/Por dialysis membrane which was bought from Spectrum labs (MWCO: 2000). Dialysis was carried out until the conductivity of water became equal to that of the pure Milli-Q water. Subsequently, the solution was dried in a vacuum at 80 °C. 1 and 2 wt % MC stock solutions were prepared by standard procedures. SDS was purchased from Fluka and used without further purification. Three different concentrations of SDS stock solutions were prepared by Milli-Q water. Different concentrations of SDS solutions were prepared by diluting the stock solutions with Milli-Q water. The cationic dye cresyl violet perchlorate (Figure 1b) was purchased from Lamda Physik and used without further purification.

**Fluorescence Correlation Spectroscopy (FCS).** The FCS experiments were carried out using a Zeiss ConfoCor 2 spectrometer. This instrument consists of an inverted optical microscope with a coverslip corrected C-Apochromat 40× water immersion objective, an argon ion laser, and a variable pinhole. For detection, an avalanche photodiode (APD) in single photon counting mode was used. This experimental setup allows FCS studies with confocal optics. Cresyl violet perchlorate (Lambdachrome, $\lambda_{exc} = 601$ nm, $\lambda_{emiss} = 632$ nm) was chosen as a dye. For excitation, the 514 nm line of the argon ion laser was used in combination with a pinhole diameter of 74 $\mu$m. The diffusion coefficients and the hydrodynamic radii were calculated on the basis of the beam waist radius calibrated by Rhodamine 6G in water (see below). The waist radius for all the measurements is $w_{xy} \approx 195$ nm. FCS measurements were performed for methyl cellulose concentrations of $c_{MC} = 0.25$, 0.50, and 1.0 wt %. The SDS concentration was varied from $c_{SDS} = 4.0 \times 10^{-4}$ to $2.0 \times 10^{-1}$ M. This concentration range covers the region below and above the classical cmc[57] of SDS. A constant cresyl violet perchlorate concentration of $c_{dye} = 10^{-8}$ M was used in all cases.

**Data Analysis.** Fluctuations in the fluorescence signal from dye molecules are quantified by temporally autocorrelating the fluorescence intensity signal. The autocorrelation functions of the measurements are evaluated by a homemade routine performing least-squares fits according to the extended autocorrelation function for the $K$ different fractions of dye molecules including triplet states.[48]

$$G(\tau) = \frac{1 + \frac{T}{1-T} e^{-\tau/\tau_{tr}}}{N} \sum_{i=1}^{K} \frac{\phi_i}{1 + \frac{\tau}{\tau_i}} \frac{1}{\sqrt{1 + \frac{\tau}{S^2 \tau_i}}} + 1 \qquad (1)$$

where $T$ is the fraction of dye molecules in the triplet state with lifetime $\tau_{tr}$, $N$ is the average number of dye molecules in the focal volume, $\phi_i$ is the fraction of the $i$th component, and $S$ is the structure parameter ($S = w_z/w_{xy}$) which describes the focal volume characterized by the radii $w_{xy}$ and $w_z$. The characteristic diffusion time of $i$th fraction $\tau_i$ is the average time required to pass the focal volume, and it is related to the diffusion coefficient $D_i$ of this fraction by the equation

$$\tau_i = \frac{w_{xy}^2}{4D_i} \qquad (2)$$

The diffusion coefficient of Rhodamine 6G in water is known as $2.8 \times 10^{-10}$ m$^2$ s$^{-1}$.[43] By using eq 2, with the experimental value $\tau_i$ and the known diffusion coefficient, the radius $w_{xy}$ is calibrated. This value of $w_{xy}$ is then used to calculate the a priori unknown diffusion coefficients of the micelles or aggregates. From the Stokes−Einstein equation we then calculate the hydrodynamic radius.

$$R_{H,i} = \frac{k_B T}{6\pi\eta D_i} \qquad (3)$$

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the viscosity of the medium.

The autocorrelation functions were fitted using eq 1 for quantitative data analysis. This procedure is performed with the Levenberg−Marquardt algorithm. The data were fitted allowing either for a single fraction of dye molecules diffusing at the same rate ($K = 1$) or for two fractions of dye molecules diffusing at different rates ($K = 2$). The former assumes that all dye molecules are in a similar environment; i.e., all dye molecules diffuse freely or all dye molecules are bound to a micelle or all dye molecules are bound to a complex of well-defined size. The latter assumes two different fractions of dye molecules bound to complexes of sufficiently different size, thereby diffusing at different average speed. In the latter case, the value of the parameter *fraction* quantifies the relative population of the different groups. An $F$-test with a 5% confidence level was applied to statistically quantify which of the two models is better suited to fit the experimental data.[49−52] All FCS measurements discussed in this paper were analyzed both by the single fraction and by the two fraction model.

The assumption that each dye diffusion time relates to a well-defined microscopic environment of the dye molecule in turn is based on the assumption that no exchange processes between the dye and different complexes happen during the observation time window. In contrast to other techniques, probing considerably longer time scales (e.g., PFG-SE NMR), this assumption seems reasonable given the short time scale probed by FCS.

**Rheology.** Rheological measurements were performed with a RFS II spectrometer from Rheometrics Scientific. A Couette system (cup diameter: 34 mm; bob diameter: 32 mm; bob length: 33 mm) was used. The sample was kept at 20 °C for half an hour and sealed to prevent the evaporation of the solvent. Steady shear flow experiments were performed from 0.02 to 1000 s$^{-1}$. The zero-shear viscosity $\eta_0$ was determined by extrapolation of the flow curves to the zero shear. The concentration of MC was $c_{MC} = 1$ wt % for all rheological measurements.

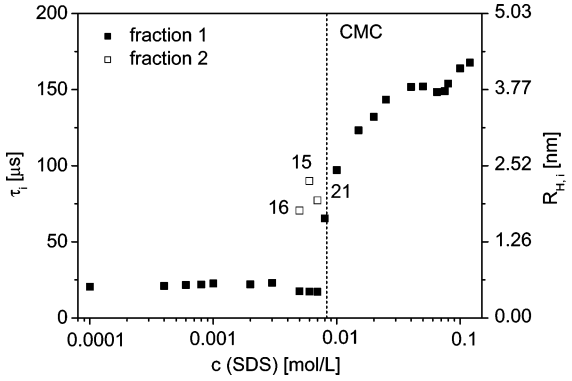


**Figure 2.** Characteristic diffusion times of cresyl violet perchlorate as a function of SDS concentration in the absence of MC. The dotted line indicates the cmc of SDS as determined by classical techniques. Only free dye molecules with ~20 $\mu$s are detected at low SDS concentration. The data result from a single-fraction fit ($K = 1$) to the autocorrelation data. A second fraction of populations with diffusion time 70 $\mu$s appears at $c_{SDS} = 5.0 \times 10^{-3}$ M. The corresponding hydrodynamic radii are shown at the right-hand axis. For the calculation of the hydrodynamic radii, the spherical micelles are assumed to diffuse in a solution of viscosity 0.001 Pa•s. The numbers refer to the population of fraction 2 in percent. The population of fraction 1 can be calculated as the complement to 100%.

## Results

Before we investigate the interactions between MC and SDS, we shall first describe FCS investigations of SDS solutions in the absence of MC. Different concentrations of SDS were measured at a constant cresyl violet perchlorate concentration of $c_{dye} = 10^{-8}$ M. This concentration relates to approximately a single dye molecule in the femtoliter-sized focal volume. The characteristic diffusion time of the dye molecules at various SDS concentrations is shown in Figure 2. At SDS concentrations below $c_{SDS} = 5.0 \times 10^{-3}$ M the diffusion time stays constant at the value observed in the absence of SDS, i.e., $\tau_{dye} = 21.5 \pm 1.0$ $\mu$s. This value relates to free dye molecules. At around $c_{SDS} = 5.0 \times 10^{-3}$ M the diffusion time significantly increases and slowly reaches $\tau_{dye}$ ~150 $\mu$s at $c_{SDS} = 4.0 \times 10^{-2}$ M characteristic of dye molecules bound to an SDS micelle. Except for the transition region, the data are best fitted by assuming a single fraction ($K = 1$) of molecules. In the range between $c_{SDS} = 5.0 \times 10^{-3}$ and $7.0 \times 10^{-3}$ M a two fraction fit yields better results, indicating that the presence of two different fractions. One fraction has the same diffusion behavior as free dye molecule, and the second is much slower and represent dye molecules bound to SDS micelles.

So far our results resemble the findings of Zettl et al. on similar surfactant systems.[46] To investigate MC/SDS interactions, we have repeated the above experiment in the presence of different amounts of MC, i.e., at $c_{MC} = 0.25$, 0.5, and 1 wt %. The SDS concentration varied between $4.0 \times 10^{-4}$ and $2.0 \times 10^{-1}$ M. The dye concentration was kept constant at $c_{dye} = 10^{-8}$ M. The results of the experiments are summarized in Figure 3. Please note that the *y*-scale of Figure 3 is considerably larger than the one in Figure 2. We start our discussion with the data obtained at the lowest MC concentration $c_{MC} = 0.25$ wt % (Figure 3A).

At low SDS concentrations, the FCS data are well represented by a single fraction fit yielding a rather constant diffusion time similar to the value observed for free dye molecules. At SDS concentrations between $c_{SDS} = 6.0 \times 10^{-3}$ and $2.5 \times 10^{-2}$ M the *F*-test indicates that a two-fraction fit is needed to reliably describe the data. A second fraction of dye molecules is observed characterized by a considerably longer diffusion time.

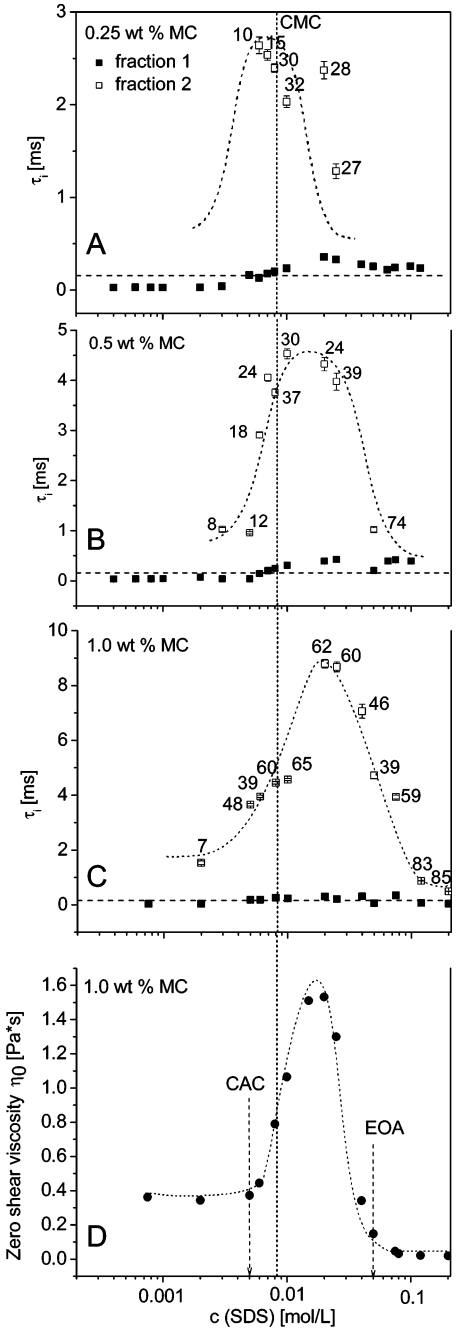


**Figure 3.** Diffusion times of the dye molecules determined for $c_{MC} = 0.25$ (A), 0.5 (B), and 1.0 wt % (C) as a function of SDS concentration. The dotted vertical line indicates the location of the cmc of SDS as determined by "classical" techniques. The dashed horizontal lines indicate the maximum diffusion time of the dye molecules with SDS in the absence of MC. Two-fraction fits ($K = 2$) are applied around the cmc. (D) Zero shear viscosity of 1 wt % MC/SDS mixtures. The critical aggregation concentration (CAC) and end of aggregations (EOA) are marked. Note that the plateau of initial viscosity is higher than the plateau after end of aggregation. The dotted curves are guides to the eye. In (A−C) the population of the fraction 2 is included (in percent). The population of fraction 1 can be calculated as the complement to 100%.

With increasing SDS concentration the diffusion time of this second fraction decreases again. Above $c_{SDS} = 2.5 \times 10^{-2}$ M the data are again well described by a single fraction fit, indicating that all dye molecules diffuse at the same time; however, a somewhat longer diffusion time as compared to the free dye molecules was observed at low SDS concentrations. At higher MC concentrations (Figure 3B,C) a similar behavior is observed. A second fraction of considerably slower dye

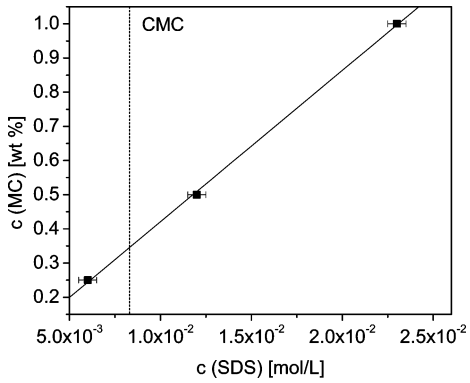


**Figure 4.** Location of the SDS concentration leading to the maximum diffusion time of the dye molecules for different MC concentration. The required amount of SDS to saturate the association is proportional to the MC concentration.

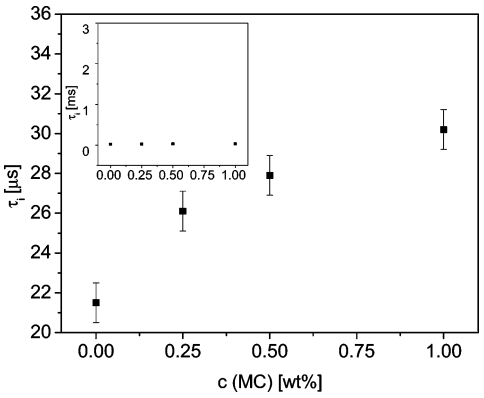


**Figure 5.** Diffusion time of dye molecules as a function of methyl cellulose concentration in the absence of SDS. The inset has the same *y*-scale as in Figure 3A for comparison.

molecules is observed around the cmc of SDS. Again, its diffusion time increases and eventually decreases again at sufficiently high SDS concentrations. We note that the location of the maximum diffusion time of this fraction shifts to higher SDS concentrations with increasing MC concentration, as can be seen in Figure 4. The concentration at which the diffusion time is maximal is roughly proportional to the MC concentration.

While FCS addresses the microscopic mobility of a single dye molecule be it free or bound to a complex, we performed rheological measurements to assess the macroscopic viscosity of the solutions (Figure 3D). Here we only concentrate on 1 wt % MC/SDS solutions. The solutions are characterized by a zero shear viscosity around 0.4 Pa·s both in the absence of SDS and at low enough SDS concentrations. At higher SDS concentration the viscosity increases significantly, reaching a maximum of around 1.53 Pa·s at $c_{SDS} = 2.0 \times 10^{-2}$ M. When the SDS concentration is further increased, the viscosity drops and eventually reaches 0.04 Pa·s at and above $c_{SDS} = 7.5 \times 10^{-2}$ M. The onset concentration at which the viscosity increases is known as critical aggregation concentration (CAC). The concentration at which the minimum viscosity is reached is denoted as end of aggregation (EOA) concentration in Figure 3D.

## Discussion

We start our discussion with the results obtained in the absence of MC. At SDS concentrations below the critical micelle concentration the dye molecules are diffusing freely without significant changes in diffusion time as a function of SDS concentration. The increasing diffusion time of the dye in SDS solutions close to the cmc indicates that the dye molecules bind to SDS micelles. The lowest SDS concentration at which the FCS autocorrelation function can be well represented by a single fraction of dye molecules bound to micelles can be defined as the cmc of SDS from FCS measurements. This value coincides with the cmc of SDS determined by "classical techniques".[57] So far our data are in line with the observation reported by Zettl et al.[46]

Before we discuss the MC/SDS mixtures, the influence of MC on the diffusion time of the dye molecules needs to be considered. Indeed, the diffusion time of the free dye molecules does increase slightly with increasing MC concentration (Figure 5). However, plotting the data on same scales as the data obtained on MC/SDS mixtures (inset to Figure 5) shows that the effect of MC is negligible when compared to the effect of SDS. The data clearly indicate that the significant change of the diffusion behavior of the dye molecules in MC/SDS mixtures is *not* induced by the presence of MC alone. One may conclude from this finding that the interaction between nonionic MC and the cationic dye is not strong enough to enable the formation of stable complexes. We note in passing that the observed small increase of the cresyl violet diffusion time is an interesting finding in itself as it suggests that the dye molecules are able to probe the presence of the MC chains even at these low MC concentrations. The finding is to some extent in contrast to earlier reports on dye labeled polymers using pyrene as a dye.[53,54] The different observation may well be due to the considerably longer lifetime of cresyl violet. This issue, however, is beyond the scope of our present study and has not been studied in more detail.

From the experiments on SDS solutions in the absence of MC (Figure 2) we know that the cresyl violet perchlorate dye behaves like a fluorescent label attached to the SDS micelles. In the presence of MC, SDS molecules are expected to form complexes with the hydrophobic zones of the MC chains by virtue of hydrophobic interactions.[12,18] Therefore, we expect to be able to follow the MC/SDS aggregates through FCS. Indeed, above the critical aggregation concentration (CAC) of SDS we find that a certain fraction of dye molecules diffuse considerably slower, indicating the formation of complexes. The absolute diffusion time of this slow fraction of dye molecules is considerably larger than the one observed for SDS micelles, indicating the formation of aggregates with rather large hydrodynamic volume. We may assume that these are aggregates between different MC chains bound together via hydrophobic interactions involving SDS molecules. We note that the rather long diffusion times may potentially lead to photobleaching of the dye during its passage time through the focal volume. This potential problem was taken care of by reducing the laser intensity and making sure that the apparent diffusion time does not depend on the laser intensity. Upon SDS binding, the hydrodynamic volume of polymer chains is expected to increase further due to the polyelectrolyte behavior.[20] The largest diffusion time is obtained at the highest MC concentration (1 wt %). Interestingly, the amount of SDS required to form maximum aggregations is proportional to the MC concentration. With higher concentration of MC, more SDS molecules are required to saturate the association as shown in Figure 4. This behavior coincides with common nonionic polymer and anionic surfactant systems.[55] The behavior of the zero shear viscosity resembles the behavior of the slowly diffusing fraction of dye molecules identified with FCS. This is in line with the notion that the macroscopic viscosity is dominated by the physical cross-links between MC chains strengthened by SDS.[56]

It is important to realize that the observed increase in diffusion time for part of the dye molecules cannot be explained by the

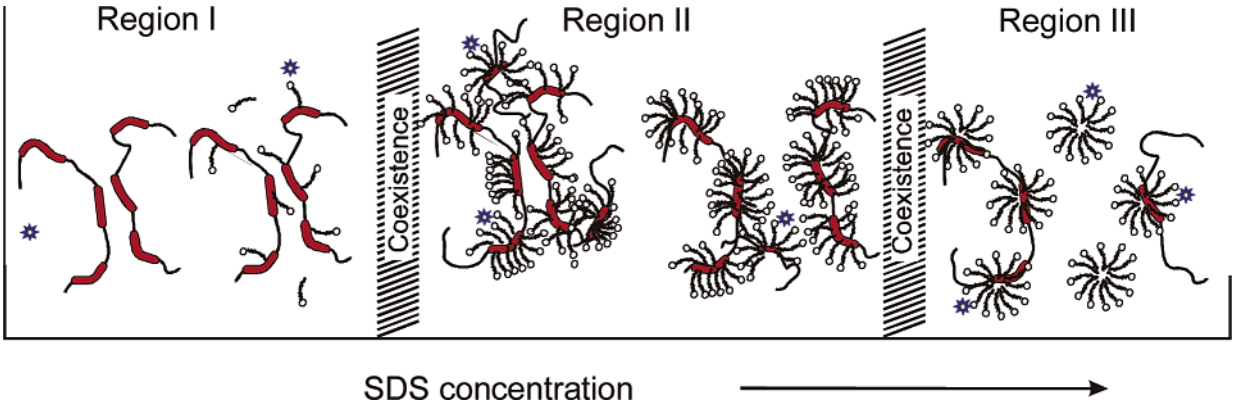


**Figure 6.** Schematic diagram explaining the MC/SDS complex formation with increasing concentration of SDS. The broader regions in the polymer chains are considered as hydrophobic regions and the remaining part as hydrophilic regions. In region I, SDS molecules are approaching hydrophobic regions of MC. Maximum aggregation and the polyelectrolyte behavior of the networks are expected in region II. In region III, the polymer chains are saturated completely with SDS micelles and the network is destroyed. Only selected hydrophobic regions are shown in region III for clarity.

increased overall viscosity. While the viscosity increases by about a factor of 4, the diffusion time of the slower fraction increases by more than a factor of 50. Therefore, even if we normalized the diffusion time of the dye by the (slightly increasing) viscosity, it still would be an order of magnitude larger than in the absence of SDS. We note that a second, considerably faster diffusing fraction of dye molecules is observed along with the large aggregates. The diffusion time of this fraction scatters slightly above the value found for dye molecules bound to SDS micelles. Here, we assume either SDS micelles or aggregates between SDS and single MC chains. The availability of single MC chain varies depending on the bulk aggregation formation with polymer and surfactant. We note that these smaller aggregates are not monitored by macroscopic techniques as they do not significantly influence the solution viscosity. Since the diffusion time is measured over shorter distances and on shorter time scales, one can easily determine the relative population of the different fractions 1 and 2. Up to the CAC of SDS 100% of the dye molecules are "free"; i.e., they are not bound to any aggregate. Above the CAC of SDS the population of larger aggregates is increasing and eventually decreases again until almost all dye molecules are bound to freely diffusing MC chains, the hydrophobic parts of which are fully decorated with SDS micelles. The relative populations are included in Figure 3 for fraction 2. The population of fraction 1 can be calculated as the complement to 100%. A complete set of all parameters is available as Supporting Information.

From the diffusion times, the diffusion coefficients of SDS micelles and MC/SDS complexes are calculated by using eq 2 (Table S-5). The diffusion coefficient of SDS micelles at the cmc is $130 \times 10^{-8}$ cm$^2$ s$^{-1}$, which is close to the literature value of $96 \times 10^{-8}$ cm$^2$ s$^{-1}$.[57] The self-diffusion constant of SDS micelles at the cmc as determined with NMR[15] is $385 \times 10^{-8}$ cm$^2$ s$^{-1}$. The hydrodynamic radii of the SDS micelles are calculated using the Stokes−Einstein equation (eq 3). They coincide with literature value (2.5 nm).[57] Spherical micelles are assumed, and the viscosity of the medium is taken as 0.001 Pa·s. The hydrodynamic radii of SDS micelles are included in Figure 2.

All MC solutions studied here are above the MC overlap concentration. Therefore, the MC chains are assumed to be part of an MC/SDS network. We do not expect isolated aggregates, and the calculation of hydrodynamic radii seems rather meaningless at concentrations below the EOA. Above the EOA concentration we can use the Stokes−Einstein equation (3) to calculate apparent hydrodynamic radii of freely diffusing MC/SDS aggregates. If we assume a spherical shape of the aggregates and a viscosity of 0.001 Pa·s, we find apparent hydrodynamic radii of some 20, 10, and 5 nm for 1.0, 0.5, and 0.25 wt % MC/SDS compositions, respectively. At 1.0 wt % MC we observe a second, slowly diffusing aggregate with an apparent hydrodynamic radius of ∼100 nm. We note that the solvent viscosity rather than the solution viscosity was used to calculate the hydrodynamic radii. The smaller aggregates are expected to diffuse rather freely in the presence of an immobilized "network" of MC/SDS complexes. We note that this effect cannot be seen by macroscopic experiments.

Our findings can be summarized by a model reported earlier for hydrophobically modified cellulose ethers/SDS systems[55] (Figure 6). We expect three regions referred to as regions I, II, and III, respectively. At low SDS concentration (region I) we expect some hydrophobic interaction between the hydrophobic regions on the MC chains with barely any influence of the surfactant. In region II complexes are formed between SDS and the hydrophobic regions of MC, leading to a significant strengthening of the physical network. As the dye molecules are known to bind to the SDS aggregates, we observe a fraction of dye molecules which diffuse considerably slower than both the free dye molecules and dye molecules bound to isolated SDS micelles. Finally, at sufficiently high enough SDS concentrations (region III) the hydrophobic regions of the MC molecules are saturated completely by SDS molecules and the physical network collapses. Consequently, the observed diffusion times decrease considerably; however, the final value is found to be longer than the one characteristic of free dye molecules. In line with this reasoning, the macroscopic viscosity first increases from region I to region II and finally (region III) drops to a value lower than in region I as even the weak physical network induced by hydrophobic interactions between MC chains are collapsed.

We may define a CAC from FCS experiments as the onset of increasing diffusion time. These CAC results happen to exactly match with the results of macroscopic techniques. In line with Diamant's theoretical predictions,[58] the value of the CAC is lower than but comparable to the cmc, and the CAC does not change significantly with the MC concentration.

## Conclusions

We have shown that a single molecule technique like FCS can be successfully used to follow the dynamics of single aggregates in polymer/surfactant systems. We can identify single interchain aggregates the hydrodynamic size of which changes

in a characteristic way as a function of surfactant concentration. These changes are reflected in the behavior of the macroscopic viscosity. The present results show the large potential of single molecule experiments as a complement to the classical macroscopic techniques for a characterization of polymer solutions and polymer/surfactant mixtures. In addition to the large aggregates dominating the macroscopic rheology of the system, the single molecule approach can identify considerably faster aggregates as well, which are not accessible by conventional techniques. Thereby the single molecule approach is able to monitor what may be called a microviscosity of the solution, i.e., the potential of small aggregates to diffuse rather fast through a network of slowly diffusing chains. This study also shows that the diffusion behavior of polymer−surfactant systems can be followed by FCS without covalent labeling with dye molecules. Moreover, FCS is only sensitive to the dye concentration; therefore, these investigations can be applied over a wide range of polymer concentrations.

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**Supporting Information Available:** A complete list of all relevant parameters presented in Tables S-1, S-2, S-3, S-4, and S-5. This material is available free of charge via the Internet at http://pubs.acs.org.

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