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Associations in Mixtures of Hydrophobically Modified Polymer and Surfactant in Dilute and Semidilute Aqueous Solutions. A Rheology and PFG NMR Self-Diffusion Investigation

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ABSTRACT: Viscosity (dilute regime) and surfactant and polymer NMR self-diffusion (dilute and semidilute regime) measurements were carried out on aqueous solutions of ethyl(hydroxyethyl)cellulose (EHEC) and of a hydrophobically modified analogue, with (HM4-EHEC) and without (HM0-EHEC) a spacer, in the presence of various amounts of sodium dodecyl sulfate (SDS). Strong polymer−surfactant interactions were revealed. From the binding isotherm the critical aggregation concentration (cac $\approx$ 3 m*m*) was obtained for the EHEC/SDS system. By comparing the results from the binding isotherms with those from the rheological measurements, molecular interactions could be correlated to macroscopic properties. The polymer self-diffusion results suggest that the spin-echo attenuation can be described by a log-normal distribution (distribution of self-diffusion coefficients), giving a median polymer self-diffusion coefficient D_{ME}. There is no difference in the trend of D_{ME} between EHEC and the hydrophobically modified analogues at various SDS concentrations. The NMR signal decays of highly viscous samples of the modified analogues are initially described by a distribution mode followed by a single exponential (slow component). The effect of hydrophobic modification is seen in the existence of a slowly diffusing component ($D_{\mathrm{net}} \approx 10^{-14}$ m^2 s^{-1}) (not observed for the unmodified analogue) that is related to a strong and long-lived network, at least of the order of the NMR time scale (ca. 0.5 s).

Introduction

It is well-known that water-soluble hydrophobically modified polymers (HM-polymers) often give a higher viscosity in solution than the corresponding unmodified polymers. Because of this higher thickening efficiency, a smaller amount of the polymer compound is needed in (technical) formulations where a certain viscosity is required. However, this is only true under certain conditions. If the HM-polymer solution is mixed with a surfactant, the viscosity enhancement due to the hydrophobic modification may be completely lost at sufficiently high levels of surfactant addition. One example of where this becomes particularly obvious is in waterborne paint formulations. For many different paint colors, a white paint is used as a base, and to obtain the desired color, a pigment paste is added. This paste contains, depending on the pigments and the manufacturer of the paste, various amounts of surfactant. Thus, the addition of additives may completely change the rheological properties of the paint formulation. Another reason for a growing use of hydrophobically modified polymers, apart from rheology control, is that their amphiphilic character suggests that they adsorb to surfaces and at interfaces. They are expected to orient in such a way that mainly the hydrophilic parts are subject to water exposure while their hydrophobic parts are directed toward the surface. This may increase the stability of particle dispersions, colloidal dispersions, or emulsions. Here a complication may be phase separation due to bridging. As indicated by the given examples, a good knowledge about physicochemical properties is required to be able to understand and prevent unwanted changes in rheology, phase behavior, etc. It is clear that the reason for the specific properties of HM-polymers is that they contain both hydrophilic and hydrophobic parts, but despite numerous investigations, neither their solution properties nor their behavior at surfaces is well understood.

Already the phase behavior is complex for amphiphilic polymers. Simulation studies[1,2] and experimental investigations[3,4] have shown that an effective attractive interaction between the polymer chains has implications for the osmotic pressure and the solubility of the polymers. If the attraction is strong enough, a phase separation may occur on dilution.[5] This (undesired) phase separation, which results in one polymer-rich and one polymer-depleted phase,[6] is opposed by the entropy of mixing. However, it has recently been found that when a hydrophobically modified polymer is mixed with its unmodified analogue, the tendency to phase separation is increased.[7,8] Here the solution separates into two phases, each containing one of the polymer components. Such a phase separation may be referred to as being segregative.[8] In fact, if the synthesis of HM-polymer results in an inhomogeneous distribution of hydrophobic tails among different polymer chains, such a phase separation may occur in solutions that are prepared of only that HM-polymer.[9] Highly substituted polymer chains are collected in one phase, while less substituted ones are found in the other phase.

Recently it has been suggested that the strength of the hydrophobic associations is modulated by surfactant addition.[5,10] The idea is that the surfactant molecules bind to the “polymeric micelles” that act as the cross-links between different polymer chains and form mixed micelles. If parts of the hydrophobic core of the poly-

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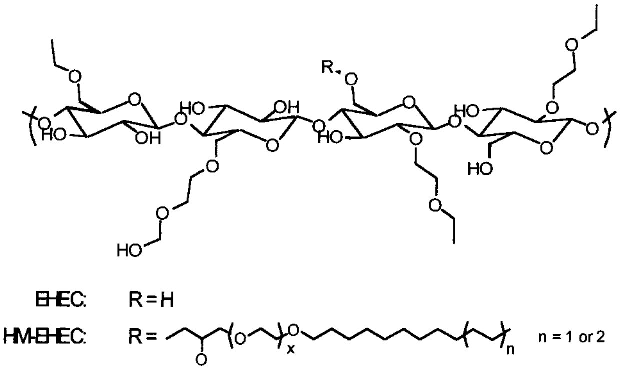

Figure 1. Schematic picture of HM0-EHEC, HM4-EHEC, and EHEC. In the unmodified variant R = H, whereas in the hydrophobically modified EHEC, R = $(CH_2CH_2O)_x-C_{14}H_{29}$. In HM0-EHEC $x = 0$ and in HM4-EHEC $x = 4$.

meric micelles still have water contact, the addition of bound surfactant molecules may help to reduce the exposure to the aqueous environment. This is probably why also ionic SDS molecules promote a phase separation at low polymer concentration.[5] The concentration of the polymer-rich phase is determined by the association strength, distance between the association points, and electrostatic swelling. For the ethyl(hydroxyethyl)-cellulose polymers, EHECs, that are used in the present investigation another factor contributing to their rich phase behavior is that their solubility in water decreases at elevated temperatures. The temperature at which this phase separation occurs is often referred to as the cloud point.

Thus, despite the lately increased knowledge about hydrophobically modified polymers, the correlation between chemical structure of the polymers and physical properties has been largely overlooked. In this investigation we therefore investigate one unmodified EHEC and two hydrophobically modified EHEC polymers, HM0-EHEC and HM4-EHEC. The EHEC differs from the HM-EHECs only by the hydrophobic modification, and the two HM-EHECs differ by that HM4-EHEC has a spacer group (four oxyethylene units) in between the hydrophobic tail and the EHEC backbone (see Figure 1). Recently, the same (HM-)EHEC systems (in the semidilute concentration regime) were investigated with rheology, intensity, and dynamic light scattering (DLS), and it was found that the dynamical properties were considerably influenced by the hydrophobic modification.[11] There was also a pronounced difference in behavior between the two HM-EHEC polymers. In 1% (w/w) aqueous solutions (without surfactant) HM0-EHEC was found to have a significantly higher viscosity than HM4-EHEC. On addition of SDS, the viscosity passed through a maximum for both the unmodified sample and the hydrophobically modified samples. The relaxation times (determined from DLS and rheology) displayed a similar behavior as the viscosity. Here the relative differences between the systems continuously became smaller, and at higher SDS concentrations, data for the EHEC, HM0-EHEC, and HM4-EHEC systems are virtually the same.

In the present investigation we have used pulsed magnetic field gradient (PFG) NMR to directly follow the self-diffusion of the polymer chains and of the SDS molecules. Our intention is to find out whether the significant differences in behavior between the EHEC systems, observed with rheology and DLS, also are reflected in the framework of this technique and whether the differences fade away at higher levels of SDS addition or, alternatively, whether a different picture emerges. From the PFG NMR data we were also able to extract the binding isotherms of SDS to all three polymers. For the sake of comparison, some rheological measurements have also been carried out on the same systems.

Experimental Section

Materials. Standard procedures were used to synthesize ethyl(hydroxyethyl)cellulose (EHEC) and the hydrophobically modified versions of EHEC (HM-EHEC). The synthesis was performed in lab scale (about 100 g batches) by Akzo Nobel Surface Chemistry AB (Stenungsund, Sweden). The degree of substitution of ethyl and ethylene oxide (EO) groups is designated DS_{ethyl} and MS_{EO}, respectively, and the three considered polymer samples have the same degree of substitution ($MS_{EO} = 1.0$ and $DS_{ethyl} = 0.8$). These notations refer to the average numbers of ethyl and EO groups per anhydroglucose unit. Since DS denotes the number of ethyl groups that have been substituted on each anhydroglucose unit, this quantity can vary between 0 and 3. Because ethylene oxide can form short oligo(ethylene oxide) chains, the molar substitution (MS) is used in this case. MS is equal to the total number of ethylene oxide groups per anhydroglucose unit and may thus exceed 3. To obtain HM-EHEC, a small amount (see below) of hydrophobic tails (a mixture of 70% (w/w) dodecanol and 30% (w/w) tetradecanol) was chemically attached to the EHEC chains. Two different versions of HM-EHEC were prepared: HM0-EHEC and HM4-EHEC. They differed by that HM4-EHEC has an extra spacer group between the EHEC chain and the hydrophobic tail. The spacer was obtained by ethoxylating the alcohol mixture, to obtain an oligo(oxyethylene) group with on average four EO units chemically attached to the alcohol molecules. A schematic representation of the three different polymers is given in Figure 1. We note that the length of the spacer may differ from that of the ethoxylation reaction depending on whether the hydrophobe binds to an activated −OH group directly on the cellulose backbone or attaches to the end of an oligo(oxyethylene) chain that already is part of the EHEC molecule. The substitution degree of hydrophobic tails, $MS_{hydrophobe}$, was determined by a procedure as given by Landoll.[12] To obtain HM0-EHEC and HM4-EHEC with the same hydrophobic modification degree ($MS_{hydrophobe} = 0.7$ mol %), which refers to the average fraction of polymer repeating units that are substituted with a hydrophobic tail, several reactions had to be performed. Prior to use, the HM-EHEC samples were purified as described elsewhere[13] and recovered by freeze-drying. To maintain a low moisture content, the purified HM-EHECs and EHEC samples were stored in a desiccator prior to use. All HM-EHECs and EHEC samples had an approximate weight-average molecular weight of $M_w \approx 100\ 000$.[14] The typical polydispersity index (M_w/M_n) of EHEC and HM-EHEC is approximately 2.[15] The overlap concentration of EHEC was estimated from the intrinsic viscosity $[\eta]$ to $c^* = 1/[\eta] \approx 0.22\%$ (w/w).

Sodium dodecyl sulfate (SDS) (specially pure) from BDH and perdeuterated SDS from Icon Services Inc. were used as supplied. To the NMR measurements heavy water (>99.8% pure) was obtained from Dr. Glaser AG.

Sample Preparation. The samples were prepared by weight from stock solutions, and to ensure complete mixing, they were allowed to equilibrate for at least 2 days on a tilting plate at room temperature before any measurements were performed. The overlap concentration estimated from the intrinsic viscosity guided us to investigate polymer concentrations corresponding to 0.1% (dilute regime) and 1% (w/w) (semidilute regime). To be able to determine the polymer self-diffusion coefficients accurately at the low polymer concentration, spectral interference from the surfactant had to be eliminated by using perdeuterated SDS. The concentrations of the samples prepared for the NMR measurements were all compensated for the higher molecular weights when perdeuterated SDS and heavy water were used.

Viscosity Measurements. Viscosity measurements of the dilute solutions (0.1% (w/w)) were performed by a glass capillary viscometer of the Ostwald type, immersed in a temperature-controlled water bath. Each measurement was made at 25 °C and performed after an equilibration time of 20 min. The measurements were repeated until three values differing less than 0.1% had been obtained. The time for water to run through the capillary was 298 s. The results are presented as relative viscosity η/η_0 (η_0 is the solvent viscosity).

In the semidilute region, the viscosity measurements were performed in the oscillatory mode with a Carri-Med controlled stressed CSL 100 rheometer, which has an automatic gap setting. Two different cone and plate geometries, 4 and 6 cm in diameter, were used for high viscous and low viscous samples, respectively. All measurements were carried out at 25 °C, and the complex viscosity (η^*) was calculated through

$$\eta^* = \sqrt{\frac{G'^2 + G''^2}{(2\pi f)^2}} \tag{1}$$

where G' is the storage modulus, G'' the loss modulus, and f the frequency. Reported viscosity values are obtained at 0.01 Hz, which corresponds to the level at the Newtonian plateau.

PFG NMR. The NMR self-diffusion experiments were performed by using the pulsed magnetic field gradient (PFG) method,[16] monitoring the ^{1}H NMR spectra using a Bruker DMX 200 spectrometer. A Bruker field gradient probe, with the capacity to deliver gradient pulses of maximum 9 T m^{-1} at a current of 40 A, was used for the diffusion measurements. Because of disturbing convection problems of low-viscous solutions at temperatures removed from the room temperature, all measurements were carried out at ambient temperature (22 °C) in 5 mm NMR tubes.

The self-diffusion coefficient of SDS was determined by an ordinary spin-echo (SE) pulse sequence.[17] The gradient pulse duration (δ) and the experimental observation time (Δ) were kept constant at 1.4 ms and 70 ms, respectively, while the gradient strength (g) was gradually increased. Because of fast T_2 relaxation (spin−spin relaxation), the polymer diffusion was measured by a stimulated echo (STE) pulse sequence.[18] In a typical experiment, δ and Δ were kept constant at values between 4 and 7 ms and 200−500 ms, respectively, while g was increased in 32 steps of 0.2 T m^{-1}. For most samples an additional measurement was performed to follow the signal decay at low k values (see below) with the same δ and Δ, whereas the gradient varied from 0 to 1 T m^{-1} in 20 steps. We always have worked in the narrow-pulse approximation, i.e., at $\delta/3 \ll \Delta$.

Analysis of Surfactant Self-Diffusion Coefficients. The PFG NMR technique is useful when studying structures and dynamics in surfactant systems.[19] Using PFG-SE-NMR or PFG-STE-NMR, the signal intensity in the case of free (Gaussian) diffusion is given by the Stejskal−Tanner equation[17]

$$I(k) = I_0 \exp(-kD) \tag{2}$$

where D is the self-diffusion coefficient and k is defined as

$$k = (\gamma g \delta)^2\left(\Delta - \frac{\delta}{3}\right) \tag{3}$$

Here, γ is the proton magnetogyric ratio ($\gamma = 2.6752 \times 10^8$ rad T^{-1} s^{-1}), δ is the duration of the gradient pulses, and Δ is the time between the leading edges of the gradient pulses. The ^{1}H signal from the surfactant displayed a single-exponential decay when the surfactant signal intensity (from the methyl group) was plotted against k in accordance with eq 2.

Analysis of Polymer Self-Diffusion Coefficients. The investigation of solutions of polymers or mixed polymer−surfactant systems with PFG NMR may be rather complex.[20] First of all, it might be difficult to obtain a well-resolved NMR spectrum because of overlapping signals due to broad signals (i.e., fast T_2 relaxation), which occur as a consequence of aggregation or specific interactions. In addition, polydisperse polymers and/or long-lived, on the NMR time scale, polymer clusters give a curved signal decay in a Stejskal−Tanner plot due to a distribution of self-diffusion coefficients. The signal intensity decays can then be interpreted in terms of a distribution of diffusing species according to

$$I(k) = \int P(D) \exp(-kD)\, \mathrm{d}D \tag{4}$$

where $P(D)$ is the normalized distribution of self-diffusion coefficients D. As in previous studies of polydisperse polymers,[21] we have assumed a log-normal distribution function

$$P(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\left(\frac{\ln(D) - \ln(D_{\mathrm{ME}})}{\sigma\sqrt{2}}\right)^2\right] \tag{5}$$

where D_{ME} is the mass weighted median diffusion coefficient and σ is a measure of the width of the distribution. It should be remarked that for eq 5 to be valid, the T_2 of the polymers must be independent of the polymer molecular weight. The latter has been shown to be a good assumption.[21,22] In solutions of associating polymers it is sometimes necessary to add a second term (slow mode) that describes slow diffusivities.[21]

$$I(k) = f\int_0^\infty P(D) \exp(-kD)\, \mathrm{d}D + (1 - f) \exp(-kD_{\mathrm{net}}) \tag{6}$$

where f is the fraction that belongs to the log-normal distribution and $(1 - f)$ is the fraction of polymer molecules that diffuses with a single diffusion coefficient D_{net}. A nonlinear Levenberg−Marquardt fitting procedure was used to obtain the adjustable parameters σ, D_{ME}, and f. D_{net} was determined from the linear part (in a semilog plot) of the signal decay and then kept fixed in the fitting procedure of eq 6.

Binding Isotherms. The observed surfactant self-diffusion coefficient D_{obs} may be interpreted as a population weighted averaged over the diffusion coefficients of the free monomeric surfactant and the polymer bound surfactant (micellized).[19] In a two-site model D_{obs} can be written as

$$D_{\mathrm{obs}} = (1 - p_{\mathrm{bound}})D_{\mathrm{free}} + p_{\mathrm{bound}}D_{\mathrm{bound}} \tag{7}$$

where p_{bound} denotes the fraction of surfactant that is bound to the polymer and D_{bound} is the diffusion coefficient of the bound surfactants. D_{bound} is given by the diffusion of the polymer. Since the polymer self-diffusion coefficient (measured in this work) is at least 1 order of magnitude lower than the diffusion coefficient of the free surfactant, the last term in eq 7 can be omitted. Actually, the change of the result by using the last term is less than 1%.

Results and Discussion

Phase Behavior. As was mentioned in the Introduction the association strength within and the electrostatic repulsion among the polymer/surfactant complexes together with the temperature-dependent solubility of the polymer chains determine the phase behavior of EHEC/SDS solutions. In an earlier investigation it was observed that when a HM-EHEC, which was hydrophobically modified with attached nonylphenol groups to the polymer backbone, was mixed with small amounts of SDS, a phase separation occurred on dilution.[5] This was not the case for the corresponding EHEC/SDS system, and the difference was ascribed to less strong hydrophobic associations with EHEC. With the present EHEC sample, which is substituted with a higher ratio of hydrophobic ethyl groups as compared to that used in the earlier investigation, a phase separation is observed with 5 m*m* SDS at a polymer concentration corresponding to 0.1% (w/w). Obviously the phase behavior of an EHEC solution is influenced by the ethyl

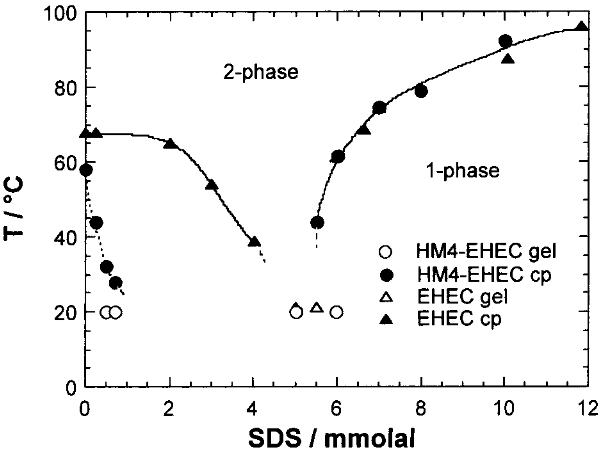

Figure 2. Phase map of aqueous mixtures of 0.1% (w/w) polymer and SDS. Circles denote HM4-EHEC and triangles EHEC. When the temperature is raised, some samples phase separate with a small gel phase (open symbols) and at higher temperatures clouding (cp) is observed (filled symbols).

and hydroxyethyl substitution. A lower substitution of hydroxyethyl groups may result in an EHEC chain that contains a larger number of patches of ethyl groups. It is reasonable that such an EHEC chain has properties resembling those of a hydrophobically modified polymer. In line with the previous investigation (HM-EHEC with attached nonylphenol groups), by modifying the EHEC with hydrophobic tails a phase separation is observed in a larger range of SDS concentration. The difference in phase behavior between EHEC and HM-EHEC is observed at low SDS concentrations, whereas at high SDS concentration the phase behavior coincides for the two systems. Figure 2 shows phase maps of EHEC/SDS and HM4-EHEC/SDS solutions at a polymer concentration of 0.1 (w/w) %. At low temperatures we observe the formation of a small gellike lump (referred to as the gel phase) at the bottom of the test tube. For EHEC it is observed at 5 and 5.5 m*m* SDS, while for HM4-EHEC the gel phase appears also for lower SDS concentrations. Especially at the intermediate SDS concentrations (5−6 m*m*) the behavior is interesting. With increasing temperature the gel phase dissolves, and the sample has a one-phase behavior before the “normal” phase separation that commonly is referred to as the clouding is observed. We believe that in both systems the gel phase appears due to hydrophobic association between stretches of the HM4-EHEC and EHEC chains that are highly substituted with hydrophobic groups, while the normal clouding phenomena at higher temperatures is due to water being a less good solvent for EHEC at elevated temperatures, giving poorer thermodynamic conditions of the systems.[23]

Viscosity. At polymer concentrations corresponding to the dilute regime, the viscosity reflects the size of polymer chains or clusters of polymer chains. On addition of SDS the relative viscosity drops at the critical association concentration, cac (Figure 3). In the calculation of the relative viscosity, the viscosity (η_0) of the corresponding SDS/water solution without polymer has been used as a reference. Our conjecture is that there exists aggregates or clusters in the solution at low surfactant concentrations. This cluster formation effect is more pronounced for the hydrophobically modified polymers. On minor addition of SDS the associations within a cluster becomes stronger, resulting in a shrinking of its size. At higher levels of surfactant addition (above the cac), the adsorption of SDS to EHEC rises, and as a result of enhanced electrostatic repulsion between polymer chains with adsorbed SDS and amended thermodynamic conditions, deaggregation of the EHEC chains occurs and the average cluster size decreases. This finding is supported by a recent dynamic light scattering study on dilute aqueous solutions of EHEC (a different batch was used) in the presence of SDS, where the hydrodynamic radius of EHEC decreased at surfactant concentrations above the cac.[24] Also, considering that the gel phase ceases at lower SDS concentration (6 m*m*) than viscosity minimum (8 m*m*), the attraction between the polymers diminishes, and larger clusters may dissolve.

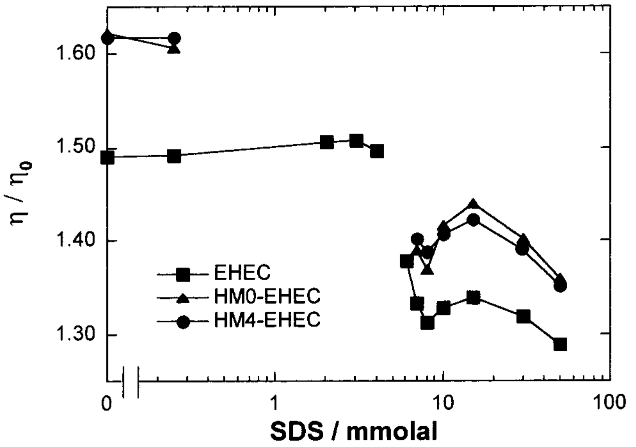

Figure 3. Relative viscosity as a function of SDS concentration in mixtures with 0.1% (w/w) EHEC (■), HM0-EHEC (▲), and HM4-EHEC (●). Note that phase separation occurs at intermediate SDS concentration.

Similar observations in viscosity behavior have previously been made for slightly hydrophobic polymers.[25,26] For both the EHEC and HM-EHEC solutions the viscosity passes a minimum at a SDS concentration corresponding to about 8 m*m* (Figure 3). At higher SDS concentrations the viscosity passes a maximum followed by a decrease. The maximum may be rationalized in the following way. The progressive binding of ionic surfactant to the polymer chains endows an apparent polyelectrolyte character to the originally nonionic EHEC, and the repulsive electrostatic forces may lead to an extension of the polymer chains. In addition, the swelling of the entities, caused by the improved thermodynamic conditions, may also contribute to this feature. At higher levels of SDS addition, electrostatic screening by free SDS molecules and SDS aggregated in free micelles results in a decrease in the viscosity. However, the fact that SDS binds to the polymer chains (see discussion below) reduces the concentration of free surfactant molecules. Consequently, the effective viscosity of the water−SDS solvent employed as reference solvent should be slightly lower. Thus, at high SDS concentrations, the curves obtained by using the corresponding water−SDS solvent viscosity represent a lower limiting case, and a true viscosity profile should exhibit a less pronounced drop.

It can be noted that the behavior of the modified and the parent polymer is similar, while the latter always gives a lower value of the viscosity than those of the HM-EHECs. If the polymers are molecularly dispersed, this would suggest that the molecular weight of EHEC is lower than that of the HM-EHECs. However, referring to the synthesis procedure, we do believe that the

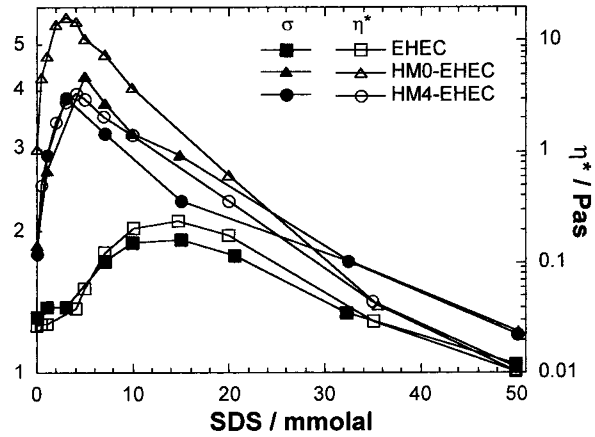

Figure 4. Complex viscosity (open symbols, right axis) and the width of the distribution σ of the diffusion coefficients (filled symbols, left axis), for 1% (w/w) polymer solutions versus SDS concentration. Squares denote EHEC, triangles HM0-EHEC, and circles HM4-EHEC.

molecular weights of the different HM-EHECs and EHEC polymers are close to each other. This is also suggested by the results presented in Figure 4, which we will return to below. Furthermore, unpublished results from static light scattering also suggest a similar molecular weight of the three different polymers.[14] Instead, we think that the observation is due to formation of aggregates or clusters composed of several polymer chains. The trend of cluster formation should be more pronounced for the hydrophobically modified polymers, and therefore higher values of the relative viscosity can be anticipated. In this context we stress that the viscosity was measured at a concentration ($c = 0.1\%$ (w/w)) not far from the overlap concentration of EHEC ($c^* \approx 0.2\%$ (w/w)). In line with the observation made in the brief study of the phase behavior (above), EHEC chains are expected to associate via the hydrophobic ethyl group. Stronger hydrophobic associations are expected for HM-EHECs, and these are manifested as a higher value of the relative viscosity at the investigated polymer concentration. Indeed, some preliminary viscosity measurements on dilute polymer solutions have shown that the intrinsic viscosity (obtained by extrapolation of the reduced viscosity curves to zero polymer concentration using the Huggins' relationship) for HM4-EHEC becomes slightly lower than that for EHEC, and a crossover is observed at ca. 0.01% (w/w) (data not shown). In this context we may note a recent viscosity study[27] on dilute aqueous solutions of EHEC (a different fraction was used) in the presence of SDS, where intermolecular associations were reported for polymer concentrations far below the overlap concentration in the presence of moderate levels of surfactant addition.

For solutions of nonassociating polymers with a concentration above c^*, the viscosity increases with concentration mainly due to entanglements of the polymer chains.[28] As several investigations have shown, a more pronounced viscosity increase takes place for the hydrophobically modified counterparts of the polymers.[29,30] Here a network may form due to associations between polymer hydrophobic tails. It is also well-known that while keeping the polymer concentration constant, a minor addition of ionic surfactant to a solution of a hydrophobically modified polymer may increase the viscosity by orders of magnitude.[31,32] The viscosity enhancement is attributed to an increased lifetime of the interpolymeric cross-links from an incorporation of surfactant molecules in the mixed micelles and to structural rearrangements so that the number of interpolymeric associations increases at the expense of intra-associations.[10,33] At further surfactant addition, the viscosity decreases when the interpolymeric cross-links are broken due to location of polymer hydrophobic tails in surfactant dominated micelles. The complex viscosity profile for the HM-EHEC/SDS system at a polymer concentration of 1% (w/w) follows that expectation (Figure 4). It can be seen that also for EHEC the complex viscosity passes through a less pronounced maximum for similar reasons as for HM-EHEC. However, there is a shift in the position of the viscosity maximum toward a higher SDS concentration value. This is due to chemical differences of the polymer chains. While EHEC is a slightly hydrophobic polymer with hydrophobic microdomains, HM-EHEC is modified with attached groups with a strong hydrophobicity. In the case of HM-EHEC the hydrophobic groups result in a surfactant binding already at very low SDS concentration (see below). As expected, if the molecular weight of the different HM-EHECs and EHEC polymers is the same, the three viscosity profiles approach each other at high SDS concentration. Here the influence of hydrophobic tails is expected to be small or negligible since most of the hydrophobic associations should be disrupted.

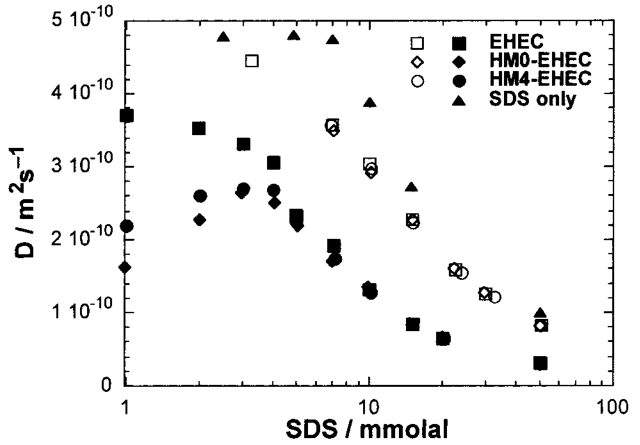

Figure 5. SDS self-diffusion coefficients in mixtures of 0.1% (w/w) (open symbols) and 1% (w/w) (filled symbols) polymer and different amounts of SDS. The SDS self-diffusion is denoted with squares for EHEC, diamonds for HM0-EHEC, and circles for HM4-EHEC. For comparison, self-diffusion of SDS without polymer from ref 35 is also presented (triangles).

Surfactant Self-Diffusion Measurements. Results from the SDS self-diffusion NMR measurements of 0.1% and 1% (w/w) polymer solutions at different SDS concentrations are presented in Figure 5. The SDS self-diffusion coefficient decreases with increasing surfactant concentration, which is due to an increasing fraction of the surfactant molecules becoming aggregated, either in free micelles or in micelles (mixed micelles) that are associated with the polymer chains. From Figure 5 it is evident that, within experimental accuracy, there is no difference in surfactant self-diffusion between dilute polymer solutions containing different HM-EHECs and EHEC polymers. Earlier investigations have shown that surfactants bind to the polymer hydrophobic tail below cac, whereas above cac the binding behavior is similar for both hydrophobically modified and unmodified polymers.[34] The similar self-diffusion coefficients of SDS are mainly due to the SDS concentrations investigated

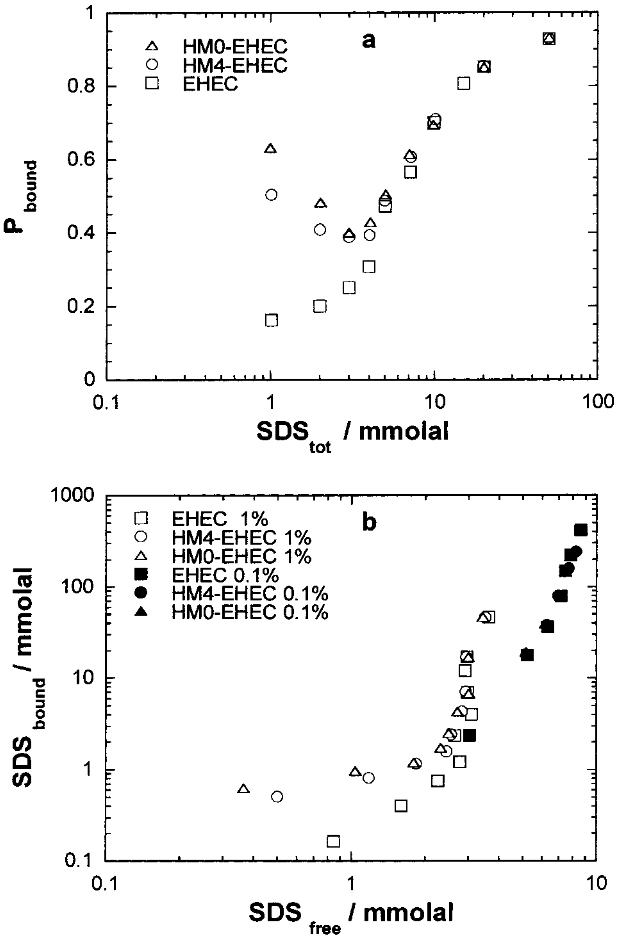

Figure 6. (a) Fraction of SDS bound to 1% (w/w) EHEC (□), 1% (w/w) HM0-EHEC (△), and 1% (w/w) HM4-EHEC (○) versus the total concentration of SDS. (b) Concentration of bound SDS in solutions of 0.1% (w/w) EHEC (■), 0.1% (w/w) HM0-EHEC (▲), and 0.1% (w/w) HM4-EHEC (●) versus the concentration of free SDS. Open symbols denote the corresponding 1% (w/w) polymer solutions.

being much higher than the concentration of polymer hydrophobic tails. (The absence of a data point at 3 m*m* SDS for the HM-EHEC solutions is due to phase separation as discussed above.)

For the SDS self-diffusion in 1% (w/w) polymer solutions, the polymer hydrophobic tails have a clear influence on the dynamics of the SDS molecules, and the surfactant self-diffusion coefficient is significantly reduced at low SDS concentration in solutions of the hydrophobically modified samples. This is due to binding of SDS to the polymer hydrophobic tails already at a very low total surfactant concentration.[35] Because of the rather low concentration of polymer hydrophobic tails (approximately 0.3 m*m* in a 1% (w/w) solution), the difference in SDS diffusion between solutions of EHEC and HM-EHEC is quickly reduced as the SDS concentration increases. The result is that the diffusion of SDS passes through a maximum in HM-EHEC solutions, while in the EHEC solution a monotonic decrease of the diffusion coefficient is observed. This decrease is, as discussed in connection with the 0.1% (w/w) solutions, due to that the fraction of SDS molecules bound to the slowly diffusing species increases.

By using eq 7, binding isotherms can be calculated from the diffusion data. The results are presented in Figure 6a, where the fraction of bound surfactant is given as a function of the total SDS concentration. As indicated already in Figure 5, the largest difference between the binding of SDS to EHEC or to the hydrophobically modified samples is observed at low SDS concentration. For the modified samples there is an SDS concentration range (up to about 3 m*m* SDS) where the binding is noncooperative. Above this concentration, the binding to the HM-EHEC samples resembles that observed for the EHEC/SDS solutions. Here the binding is cooperative. A strong evidence for a two-step binding process for the HM-EHEC samples is the dip in the fraction of bound surfactant, which defines the crossover between the noncooperative and the cooperative binding processes. For EHEC the binding is much less pronounced at low SDS concentrations but still significant.

Previously, we have shown that, in line with observations for several other polymer/surfactant systems, mixed micelles containing both SDS and EHEC are formed. The surfactant aggregation number of these mixed micelles is in the range $N_{\mathrm{agg}} = 20-40$ and increases with surfactant concentration.[35] Often this binding process is quantified by a critical aggregation concentration (cac). By defining cac as the concentration of free surfactant that is not exceeded in the concentration range where the polymer chains are not saturated with surfactant molecules, we find cac $\approx$ 3 m*m* for the EHEC/SDS system (Figure 6b). Because EHEC is likely to have hydrophobic patches and may be viewed as a hydrophilic polymer modified with small hydrophobic groups, a small fraction of SDS binds to the EHEC chains already well before the cooperative process sets in at a total SDS concentration of 4 m*m*. At higher SDS concentrations there is no difference in binding behavior between EHEC and the HM-EHEC samples.

Figure 6b also includes data from solutions that contain 0.1% (w/w) HM-EHEC and EHEC. From these data it seems that the binding process is also influenced by the polymer concentration. It seems that the number of surfactant molecules that can bind to the EHEC chains becomes smaller when the polymer concentration decreases.[36] A saturation of the polymer chains is indicated by the concentration of free surfactant approaching the cmc (in the case of SDS cmc $\approx$ 8 m*m*). In the evaluation of diffusion data at this stage, we have to take into account the diffusion of free surfactant micelles, and eq 7 is no longer valid.

Polymer Self-Diffusion Measurements. When it comes to the polymer self-diffusion, we will start by discussing the mean value D_{ME} (the fast mode) that is obtained from the log-normal distribution of diffusion coefficients (see eqs 4−6). In the dilute regime the polymer self-diffusion may reflect the effective size of the polymer chains or clusters. In the limit of zero concentration, the diffusion coefficient is inverse proportional to the hydrodynamic radius R_{H} of a spherical species according to the Stokes−Einstein relation $D = k_{\mathrm{B}}T/6\pi\eta_0 R_{\mathrm{H}}$, where k_{B} is the Boltzmann constant and η_0 is the viscosity of solvent at temperature T. A faster diffusion would then imply a smaller effective radius of the aggregates. Thus, in line with the interpretation of the viscosity data, initially, an addition of SDS to the dilute solutions increases the polymer self-diffusion because the size of the polymer−surfactant complexes decreases due to disruption of the clusters. As expected from the lower viscosity of EHEC, the values of the polymer self-diffusion coefficient are higher than those of the HM-EHEC samples. However, at high SDS concentration the difference between the values of the

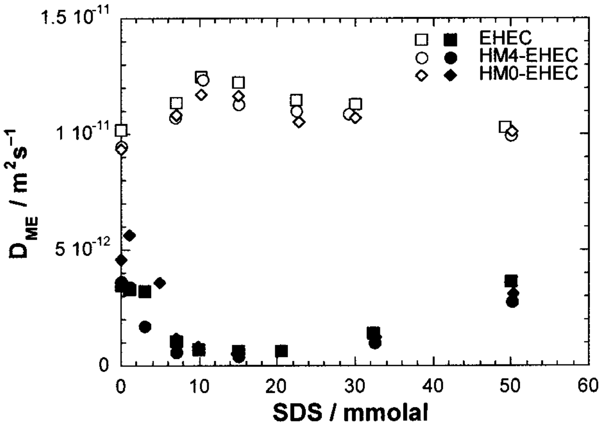

Figure 7. Median polymer self-diffusion coefficients in mixtures of 0.1% (w/w) (open symbols) and 1% (w/w) (filled symbols) polymer and different amounts of SDS. The polymer self-diffusion is denoted with squares for EHEC, diamonds for HM0-EHEC, and circles for HM4-EHEC.

diffusion coefficient fades away. At higher SDS concentrations the diffusion seems to decrease slightly. This effect might be due to electrostatic repulsion between the mixed micelles and/or the free micelles, analogous to the decrease in diffusion coefficient observed in binary ionic surfactant–water systems containing micelles.[37] Another effect that may contribute to this behavior is that the "effective" solvent viscosity increases at high levels of SDS addition.

From Figure 7 it follows that there is a decrease in the diffusion coefficient for the 1% (w/w) polymer solutions within virtually the same SDS concentration range as a maximum in the diffusion coefficient is observed for the 0.1% (w/w) polymer solutions. The reason for the decrease is likely to be interpolymeric associations that increase in number and/or strength. Thus, in the 0.1% (w/w) solutions the molecules and clusters act virtually as individual units, while in the 1% (w/w) solutions associations between different polymer chains or clusters become important. A closer examination reveals that the extreme values in polymer diffusion (minimum for 1% (w/w) and maximum for 0.1% (w/w)) are located at slightly different SDS concentrations. This is because a larger number of surfactant molecules can bind to polymer chains in the 1% (w/w) samples.[36]

An important observation, that we have neglected so far, is that the trends in D_{ME} are the same independent of whether the polymer chains are hydrophobically modified or not. In the 1% (w/w) polymer solutions this stands in contrast to the viscosity profiles (Figure 4) for which the changes are larger and are located within a more narrow SDS concentration range for the HM-EHEC/SDS systems. On the other hand, the changes in the polymer diffusion data seem to coincide with the SDS concentration ranges where the changes in viscosity are observed in the EHEC/SDS system. To get a deeper understanding of these observations, we will take a closer look on the signal decays of 1% (w/w) EHEC, HM0-EHEC, and HM4-EHEC solutions at different SDS concentrations.

As we can see from Figure 8a–c, there is a curvature when the decays are plotted in a Stejskal–Tanner representation. This is an indication of that the sample contains a distribution of species with significantly different diffusion coefficients. The signal decays for both the EHEC-SDS solutions and the HM-EHEC solutions in the presence of high levels of SDS addition are well described by eq 4 (Figure 8), where a log-normal distribution function has been used. A fit to the signal decay gives the width of the distribution σ and the mass-weighted median diffusion coefficient D_{ME}. For the HM-EHEC solutions, the curvature in Figure 8 becomes much more pronounced in the SDS concentration range between 1 and 15 m*m* than for the corresponding EHEC-SDS solutions and, moreover, flattens out to a linear decay (exponential decay) at higher k values. The signal decays in those cases cannot be described by eq 4 but have to be analyzed in the framework of eq 6. In

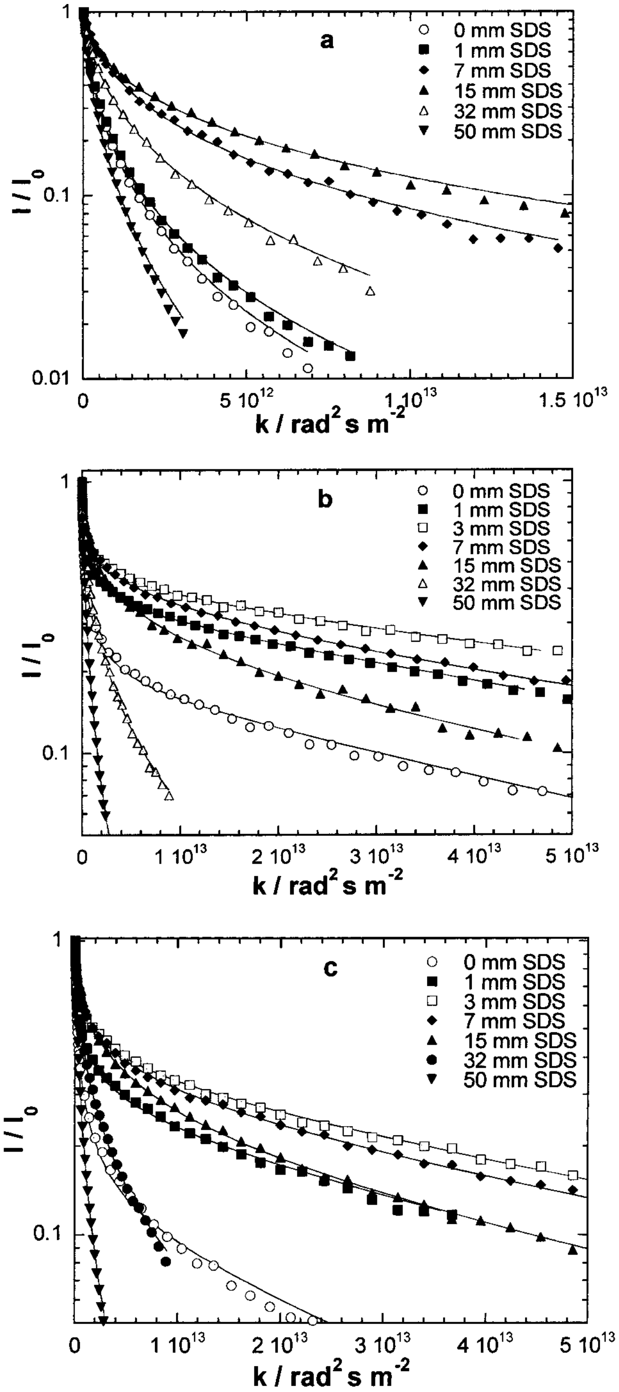

Figure 8. Signal decays for 1% (w/w) polymer solutions in the presence of various amounts of SDS. The concentrations of SDS in mmolal are displayed in the legend. (a) EHEC: The lines are best fits of eq 4 to the data. (b) HM0-EHEC: The lines are best fits of eqs 4 and 6 to the data. (c) HM4-EHEC: The lines are best fits of eqs 4 and 6 to the data.

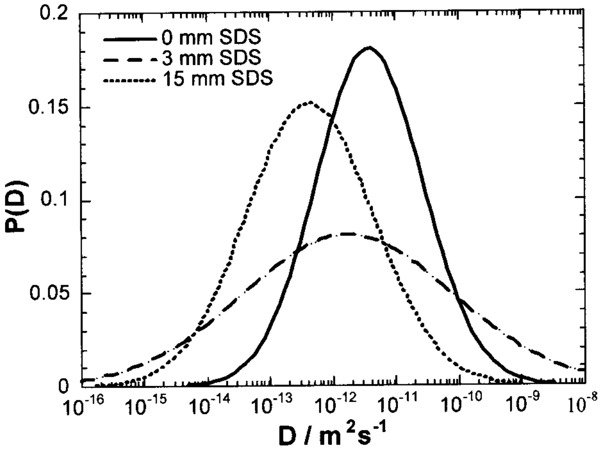

Figure 9. Example of the probability of different diffusion coefficients as obtained from σ if a log-normal distribution is used. This picture represents mixtures of 1% (w/w) HM4-EHEC and 0, 3, or 15 m*m* SDS.

eq 6, the second mode corresponds to an extra self-diffusion coefficient, D_{net}.

The widths of the distribution of mass-weighted median self-diffusion coefficients σ correlate very well with the profiles displayed by the complex viscosity at the different SDS concentrations (Figure 4). From Figure 4 it is also clear that σ assumes much higher values in the case of HM-EHEC, and the maximum of the peak is shifted toward lower SDS concentration. The high values give a very broad distribution of diffusion coefficients with values of the diffusion coefficients that are somewhat unreasonable (Figure 9). We do not see the same behavior for the lower polymer concentration (i.e., 0.1% (w/w)) where the value of σ is approximately 0.9 (within the experimental error) over the entire concentration regime of SDS (the results are not shown here). The high values of σ in the semidilute regime cannot be accounted for by a high polydispersity in molecular weight, since the values of σ are much lower at high SDS concentration and in dilute polymer solutions. A broad distribution (curvature) has previously been attributed to a combined effect of polydispersity in molecular weight and associations of the polymer chains.[21,38] Furthermore, a strong scaling of the molecular weight on the diffusion coefficient is expected when the polymer chains diffuses in a static, heterogeneous matrix.[39,40] In fact, by a previous study, performed by DLS on the same systems, we were able to determine the heterogeneity of the systems.[11] The result is that the systems are most heterogeneous in the region where we observe the increase and maximum in σ and the viscosity of the HM-EHEC polymers. The fact that the echo attenuations reveal very broad distributions of self-diffusivities and that σ correlates well with the viscosity enhancements of the systems but not with the molar mass distribution width of the polymers suggests that cluster formation is a strong candidate for this behavior. In this context we may note a recent theoretical study[41] in the Rouse–Zimm (unentangled regime), where dynamical properties of reversible networks formed in solutions of associating polymers were considered. It was argued that the dynamics is governed primarily by the network strand size and by the effective lifetime of reversible junctions.

For the EHEC system, D_{ME} displays its minimum value at the same concentration of SDS as where we observe the extreme values of σ and the viscosity (cf. Figures 4 and 7). As seen from Figures 4 and 7, this is not the case for the HM-EHEC systems. However, in the viscous samples of HM-EHEC a slow component is also found. This diffusion coefficient (D_{net}) can be as low as 10^{-14} m^2 s^{-1}. The fraction of the slow component, (1 − *f*), increases with increasing solution viscosity, whereas D_{net} decreases (Figure 10). It is obvious that the largest impact of the slow diffusion mode is detected at the surfactant concentration where the viscosity enhancement of the systems is at its optimum. These results suggest that the slow diffusive mode only appears in systems where strong associations reign. We may also note (Figure 10) that the values of D_{net} are higher for the HM4-EHEC/SDS system than for the HM0-EHEC/SDS system. This trend is consistent with the behavior expected in the light of the complex viscosity results (see Figure 4). The slow migrations suggest a long-lived relaxation process, which may be related to the disengagement of polymer chains from the transient network and may reflect the effective lifetime of reversible junctions.

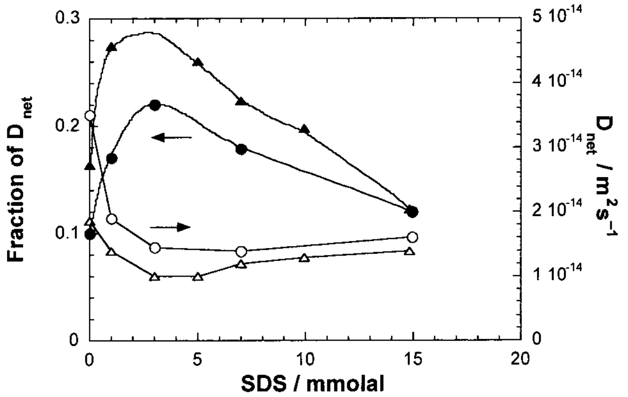

Figure 10. Fraction of the slow diffusion coefficient in eq 6 (left axis, solid symbols) and the diffusion coefficient of the slow component D_{net} (right axis, open symbols) in solutions of 1% (w/w) HM0-EHEC (triangles) and 1% (w/w) HM4-EHEC (circles) at various SDS concentrations. The solid curves are only guides for the eye.

Concluding Remarks

We have found that in solutions of EHEC and HM-EHEC polymers in the presence of SDS a phase separation is observed at low polymer concentrations and low temperatures. The attraction between the polymer chains varies with the SDS concentration, and the phase separation is only observed within a limited SDS concentration range. On increasing the temperature the solution may pass through a one-phase behavior before the normal clouding phenomenon is observed. From the PFG NMR measurements it is interesting to see that the fits of the echo decays suggest two different self-diffusion modes in the solutions of HM-EHEC with SDS additions that give high viscosity. At these conditions, the slowest dynamics is expected, and a slow diffusion mode appears as a single-exponential signal decay at high *k* values. In combination with information from rheological measurements on the same systems, we suggest that the fast diffusion mode (D_{ME}) is related to the diffusion of HM-EHEC and EHEC chains in a network that is held together by entanglements and hydrophobic associations. We also suggest that the slow diffusion mode (D_{net}) originates from the long-lived associations that are formed in solutions of the hydrophobically modified polymers. Possibly the strongly bound HM-EHEC chains form a transient network. Thus, the polymer dynamics is largely influenced by the strength of the associations. The NMR data suggest that SDS molecules bind to the EHEC and HM-EHEC chains and form mixed micelles. From our data we obtained binding isotherms for 1% (w/w) polymer solutions, in good agreement with previously published isotherms. The general picture that emerges from this work is that addition of an ionic surfactant induces interactions that are more pronounced, and the interaction peak is located at a lower level of SDS addition for the HM-EHEC/SDS systems than for the EHEC/SDS system. These associations give rise to very broad distributions of polymer self-diffusivities, and the PFG NMR results reveal essential differences in diffusion behavior between systems containing unmodified and hydrophobically modified polymers.

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