

## Effect of Hydrophobic Modification of a Nonionic Cellulose Derivative on the Interaction with Surfactants. Rheology

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The interactions between various surfactants (anionic, cationic, and nonionic) and a nonionic ethyl(hydroxyethyl)cellulose (EHEC) polymer or a hydrophobically modified analogue (HM-EHEC) have been examined. The study has been performed as a comparative investigation between the hydrophobically modified polymer and the unmodified parent polymer using rheology. The rheological results have been analyzed with the aid of a simple modified Maxwell model. Information about the low-frequency behavior was extracted from this model, and the rheological features were presented in terms of the complex viscosity and a characteristic relaxation time. In the presence of an ionic surfactant, the rheological measurements revealed significant polymer/surfactant interaction for both EHEC and HM-EHEC, but the interaction peak, observed in the different rheological quantities, was more pronounced and located at a lower surfactant concentration for the hydrophobically modified polymer. In the presence of a nonionic surfactant, the polymer/surfactant interaction was weaker. By considering the temperature effect, an important difference in the polymer dynamics between the hydrophobically modified polymer and the unmodified analogue was established. The hydrophobically modified polymer shows a normal temperature dependency, while the motion of the unmodified analogue is slowed down with increasing temperature. The finding for the unmodified polymer is attributed to increased polymer/polymer attractions with an increased temperature. It has also been shown that the hydrophobically modified polymer has features regarding the formation and breakdown of the polymer/surfactant complex in common with other hydrophobically modified polymers (both nonionic and ionic). At a certain surfactant concentration the network starts to lose its connectivity, however, because of an increased surfactant aggregation number of the mixed micelles, the breakdown process is postponed when the surfactant chain length is increased.

### Introduction

Complex water-based systems containing hydrophobically modified polymers and surfactants find important practical applications in various domains such as detergency, paints, cosmetics, oil recovery, etc.<sup>1–5</sup> Essentially, these polymers consist of a long-chain hydrophilic backbone to which small amounts of hydrophobic substituents<sup>6</sup> are incorporated through chemical grafting. Hence, these polymers comprise both hydrophilic and hydrophobic parts and exhibit an amphiphilic behavior in aqueous solutions. When these polymers are dissolved in water, the hydrophobic groups aggregate to minimize their exposure to water, in a fashion analogous to that of surfactants above the critical micelle concentration.

One of the most important practical aspects of hydrophobically modified polymer and surfactant systems is the possibility to control rheology<sup>1,4</sup> over very wide ranges. In semidilute aqueous solutions of hydrophobically modified polymers in the presence of a moderate amount of surfactant, three-dimensional network structures may form,<sup>1</sup> while at high surfactant concentrations, the polymer network is disrupted.<sup>7,8</sup> The process of formation and breakdown of the network has often been followed by measuring rheology, because the rheological characteristics are strongly dependent upon the actual levels of surfactant addition.

In the present paper, we report the effects of various ionic and nonionic surfactants on the rheological properties of

semidilute aqueous solutions of ethyl(hydroxyethyl)cellulose (EHEC) and of a hydrophobically modified analogue (HM-EHEC). The results from the present oscillatory shear measurements were interpreted with the aid of a modified Maxwell model. Furthermore, by considering the temperature effect on rheological parameters, an important difference between the hydrophobically modified polymer and the unmodified analogue could be revealed. The aim of this study is to gain a deeper insight into the mechanisms that govern the rheological features of polymer/surfactant associations.

### Experimental Section

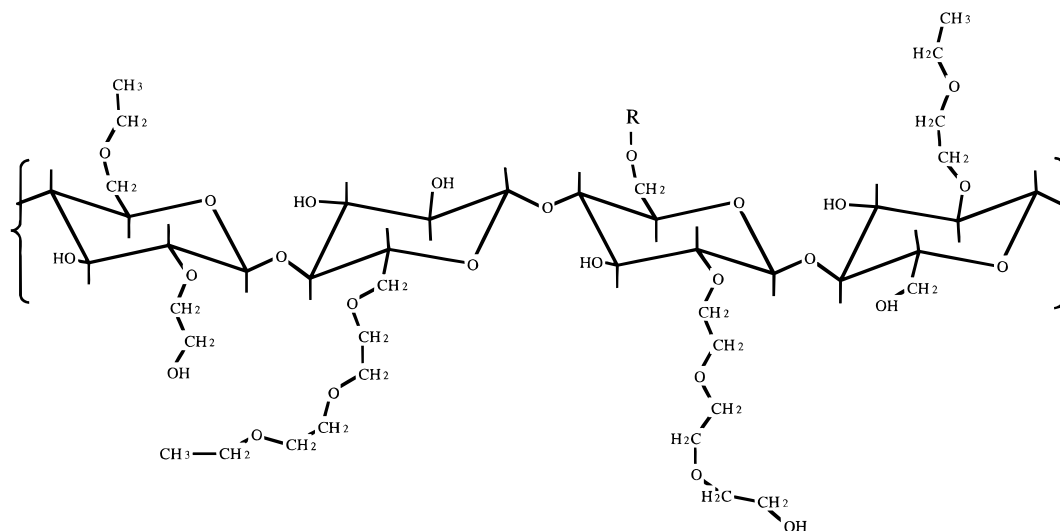
**Materials.** The polymers were manufactured by Akzo Nobel Surface Chemistry AB and received as a kind gift. Both the unmodified and the hydrophobically modified polymer (HM-polymer) are ethyl(hydroxyethyl)cellulose ethers (EHECs) with the same average molecular weight ( $M_w \approx 100\,000$ ) and degrees of ethyl and hydroxyethyl substitutions,  $DS_{\text{ethyl}} = 0.6–0.7$  and  $MS_{\text{EO}} = 1.8$ , respectively. The DS and MS values correspond to the average number of ethyl and hydroxyethyl groups per repeating anhydroglucose unit of the polymer. The values of  $M_w$ ,  $DS_{\text{ethyl}}$ , and  $MS_{\text{EO}}$  were all given by the manufacturer. The hydrophobic modification consists of a low number of non-ylphenol groups grafted to the polymer backbone. The degree of HM-modification was measured by UV absorbance of the aromatic ring at 275 nm using phenol in aqueous solution as a reference. It was determined to 0.64 mm in a 1 w/w% polymer solution. The number suggests a HM-modification of 1.7 mol % and corresponds to an average value of about 6.5 HM-groups per polymer chain. In Figure 1, a schematic picture of the

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EHEC: R = H

HM-EHEC: R =  $-(\text{CH}_2\text{-CH}_2\text{O})_x\text{-C}_6\text{H}_4\text{-C}_9\text{H}_{19}$

**Figure 1.** The structure of the polymers in a schematic representation. For HM-EHEC the hydrophobic side-group, R, is a branched nonylphenol.

**TABLE 1: Approximate cmc Values of the Surfactants Used in the Present Investigation<sup>a</sup>**

surfactant	cmc (mM)	surfactant	cmc (mM)
SDS <sup>a</sup>	8.2	C <sub>18</sub> TAC <sup>a</sup>	0.34
SOBS <sup>b</sup>	11.4	C <sub>12</sub> E <sub>5</sub> <sup>a</sup>	0.057
C <sub>12</sub> TAC <sup>a</sup>	20	C <sub>12</sub> E <sub>8</sub> <sup>a</sup>	0.071
C <sub>16</sub> TAC <sup>a</sup>	1.3		

<sup>a</sup> From ref 23. <sup>b</sup> From ref 24.

polymers' chemical structures is given. Before use, the polymers were purified as described elsewhere<sup>9</sup> and stored in a dessicator prior to use.

The surfactants (sodium dodecyl sulfate, SDS, sodium octyl benzene sulfonate, SOBS, *n*-alkyltrimethylammonium chloride, C<sub>n</sub>TAC, and oligoethylene glycol monododecyl ether, C<sub>12</sub>E<sub>n</sub>) were all of high quality, and used as received without any further purification (see Table 1). Samples were prepared by weighing aliquots from stock solutions and mixed by turning end over end at room temperature for several days. For all samples, water of Millipore quality was used.

**Rheology Measurements.** In the rheological measurements, a Bohlin VOR constant strain rheometer was utilized. The rheometer was equipped with a circulating water bath to control the temperature to within  $\pm 0.1$  °C. The measurements were performed with the rheometer put in the oscillatory mode with a double-gap geometry used for the low-viscous samples and an ordinary cup and bob geometry for the samples with higher viscosity. All rheological data were checked as a function of strain amplitude to ensure that the measurements were performed in the linear viscoelastic region.

## Results and Discussion

**Analysis of the Rheological Data.** In an earlier publication<sup>8</sup> we noted that the loss modulus,  $G''$ , as a function of the storage modulus,  $G'$ , gave for the (HM-)EHEC/SDS systems a linear relation in a log-log plot. The exponent  $e$  ( $G'' \sim (G')^e$ ) was found to vary with addition of SDS and to pass through a maximum approximately at the same surfactant concentration as the dynamic viscosity, but no closer analysis was presented. First, we will recapitulate some general features of viscoelastic solutions.

In a system that can be described by a single Maxwell element (a spring and a dash pot in a series),  $G'$  and  $G''$  can be

written<sup>10</sup>

$$G'(\omega) = G_{\infty} \frac{\tau^2 \omega^2}{1 + \tau^2 \omega^2} \quad (1)$$

$$G''(\omega) = G_{\infty} \frac{\tau \omega}{1 + \tau^2 \omega^2} \quad (2)$$

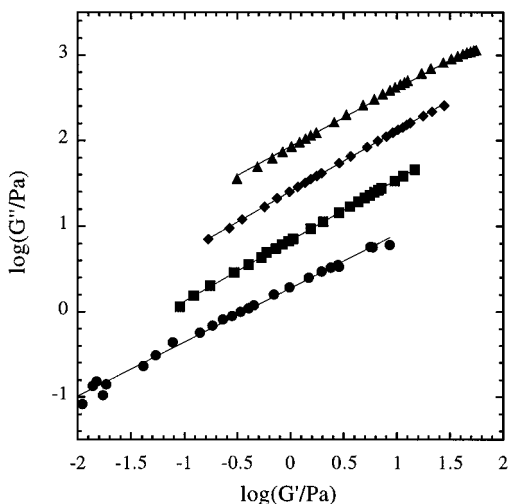
Where  $G_{\infty}$  represents the plateau value of  $G'$  at high frequencies,  $\tau$  is the specific time of the relaxation process, and  $\omega$  is the angular frequency (rad/s). If the two relationships are combined to eliminate  $\tau \omega$ ,  $G''$  can be expressed in terms of  $G'$  as

$$G''^2 = G'(G_{\infty} - G') \quad (3)$$

which can be written as

$$\log(G'') = \frac{1}{2} \log(G') + \frac{1}{2} \log(G_{\infty} - G') \quad (4)$$

Provided that  $G' \ll G_{\infty}$  eq 4 suggests that, in a log-log plot, the scaling exponent should equal  $e = 0.5$  for the Maxwell model. However, as mentioned above, experimental data<sup>8</sup> on semidilute solutions of HM-EHEC in the presence of SDS showed that the exponent in general differs from this value, Figure 2. Often, and also in the present investigation, rheology data of polymer solutions are poorly reproduced by assuming one single relaxation process. The  $G'$  and  $G''$  data for one specific polymer solution (1 w/w% HM-EHEC with 2 mM SDS measured at 25 °C) are depicted in Figure 3a. The data are fitted to the sum of one, two, three, or four Maxwell elements with different relaxation times. The fits of  $G'$  and  $G''$  are improved as the number of Maxwell elements increase, suggesting that the system is described by a distribution of relaxation times. A plot of  $\log(G'')$  as a function of  $\log(G')$  for the double Maxwell model fitted to the experimental data generates a value of  $e = 0.620$ , which should be compared to a value of  $e = 0.710$  for the experimental data (see Figure 2). The increase of the exponent  $e$  from 0.5, as in the single Maxwell model, can thus be traced to a change in the number of relaxation modes (or a change in the relative strengths of the associations giving rise to the different relaxation modes).



**Figure 2.** Plot of  $\log(G'')$  as a function of  $\log(G')$ . The exponent  $e$  ( $G'' \sim (G')^e$ ) assumes the values 0.598 (●), 0.710 (■), 0.709 (◆), and 0.658 (▲), for the systems 1 w/w% HM-EHEC/0 mm SDS, 1 w/w% HM-EHEC/2.0 mm SDS, 1 w/w% HM-EHEC/4.5 mm SDS, and 1 w/w% HM-EHEC/10.0 mm SDS, respectively. The three upper curves have been vertically shifted by adding 0.5, 1.0, and 1.5, respectively, and the full lines describe the best linear fits to the data.

Replacing 0.5 in eq 4 with  $e$ , as suggested by experimental data, eqs 1 and 2 can be written as

$$G'(\omega) = G_{\infty} \left( \frac{\tau^2 \omega^2}{1 + \tau^2 \omega^2} \right)^{1/2e} \quad (5)$$

$$G''(\omega) = G_{\infty} \frac{\tau \omega}{1 + \tau^2 \omega^2} \quad (6)$$

In analogy with the transformations of eqs 1 and 2 into eq 4, eqs 5 and 6 can be written as

$$\log(G'') = e \log(G') + (1 - e) \log(G_{\infty}) \quad (7)$$

provided  $G'^{2e} \ll G_{\infty}^{2e}$ . The slope of the line describing the relationship between  $\log(G')$  and  $\log(G'')$  equals  $e$ , and the intercept can be used to evaluate  $G_{\infty}$ .

An analysis of the slopes, in the linear regime at low frequencies, of  $\log(G')$  and  $\log(G'')$  as a function of  $\log(\omega)$  (see Figure 3a) gives values of 1.1 and 0.8, respectively. The corresponding values for a Maxwell model is 2 and 1, and therefore  $e$  is introduced in eq 5.

In Figure 3b the experimental data for the system 1 w/w% EHEC/12.9 mm SDS at 25 °C is given. The parameters  $e$  and  $G_{\infty}$  have been obtained from a fit to eq 7, and the upper set of curves are determined from eqs 5 and 6 by fitting the characteristic time,  $\tau$ , to the data. Figure 3c shows the corresponding plot for 1 w/w% HM-EHEC/2.0 mm SDS at 25 °C. As a comparison the best fit of a Maxwell element is included in the figures ( $e = 0.5$ ). As shown by Figure 3 the description of experimental data is much improved by increasing the value of the exponent  $e$  from 0.5. We should note that the present rheometer setup only allows us to measure the low-frequency end of the mechanical spectra, in the oscillatory shear mode, and the introduction of the exponent  $e$  in the Maxwell model should be seen as a first attempt to represent the spectra of relaxation times.

Before we discuss the results in detail we will recapitulate some general differences between EHEC and HM-EHEC in solution upon addition of surfactant. Specific batches of EHEC are known to form thermoreversible gels when they are mixed with ionic surfactants.<sup>11–14</sup> In these semidilute systems, it has

been argued<sup>15</sup> that the gelation properties are governed by the interplay between swelling (caused by the ionic surfactant) and connectivity (established by “lumps” or hydrophobic associations). The hydrophobic regions become gradually more hydrophobic as the temperature increases and the general idea is that the connectivity given by the “lumps” is strengthened by temperature at low surfactant concentration. The swelling capacity is expected to increase with increasing surfactant concentration. At sufficiently high surfactant concentration the connectivity of the network is disrupted due to dissolution of the “lumps”. The tendency of gel formation of these EHEC/ionic surfactant systems is dependent on the arrangement of hydrophobic patches separated by intermediate hydrophilic parts along the polymer chain. There are also EHEC samples in which these more distinct hydrophobic patches are not present, but rather the hydrophobic groups are more or less smeared out along the chain. In these samples, microphase separation and formation of “lumps” is less favored and therefore they do not form thermoreversible gels. The EHEC sample used in the present investigation is of this class. When it comes to HM-EHEC, a quite different situation emerges. In this case the polymer can be characterized as the ultimate example of a blocky structure. In this system, in contrast to the EHEC polymer, we have specific hydrophobic interaction sites for surfactant binding which can act independent of temperature. The binding induces formation of mixed micelles between polymer hydrophobic tails and surfactants. Furthermore, the hydrophobic tails grafted to the HM-EHEC backbone can induce cross-links between different polymer chains.

Piculell et al.<sup>16</sup> have suggested that the maximum strength and the breakdown of a network of a hydrophobically modified polymer has universal features, and substantial insight was gained by analyzing rheological data in the framework of the binding isotherm of different surfactants to various hydrophobically modified polymers. The total surfactant concentration at the point of maximum viscosity of the polymer/surfactant mixture,  $c_{s,max}$ , was argued to be correlated to the onset of loss in connectivity of the network. This concentration is correlated to the cooperative part of the binding isotherm,<sup>17</sup> and therefore the mixed micelles begin to be related to micelles formed in absence of polymer hydrophobic tails (the surfactant dominates the mixed micelles). The free surfactant concentration,  $c_{s,f}$ , at this point was found to be correlated to the “relevant cmc” of the surfactant,  $cmc_s$ , which corresponds to the surfactant critical micelle concentration (cmc) if the polymer backbone itself is inert and to the critical aggregation concentration ( $cac$ ), which is lower than cmc, if the parent polymer interacts with the surfactant. Thus, at  $c_{s,max}$ , the reduced free surfactant concentration,  $\gamma = c_{s,f}/cmc_s$  was found to be close to unity.<sup>16</sup> It was suggested that  $c_{s,max}$  may be expressed as

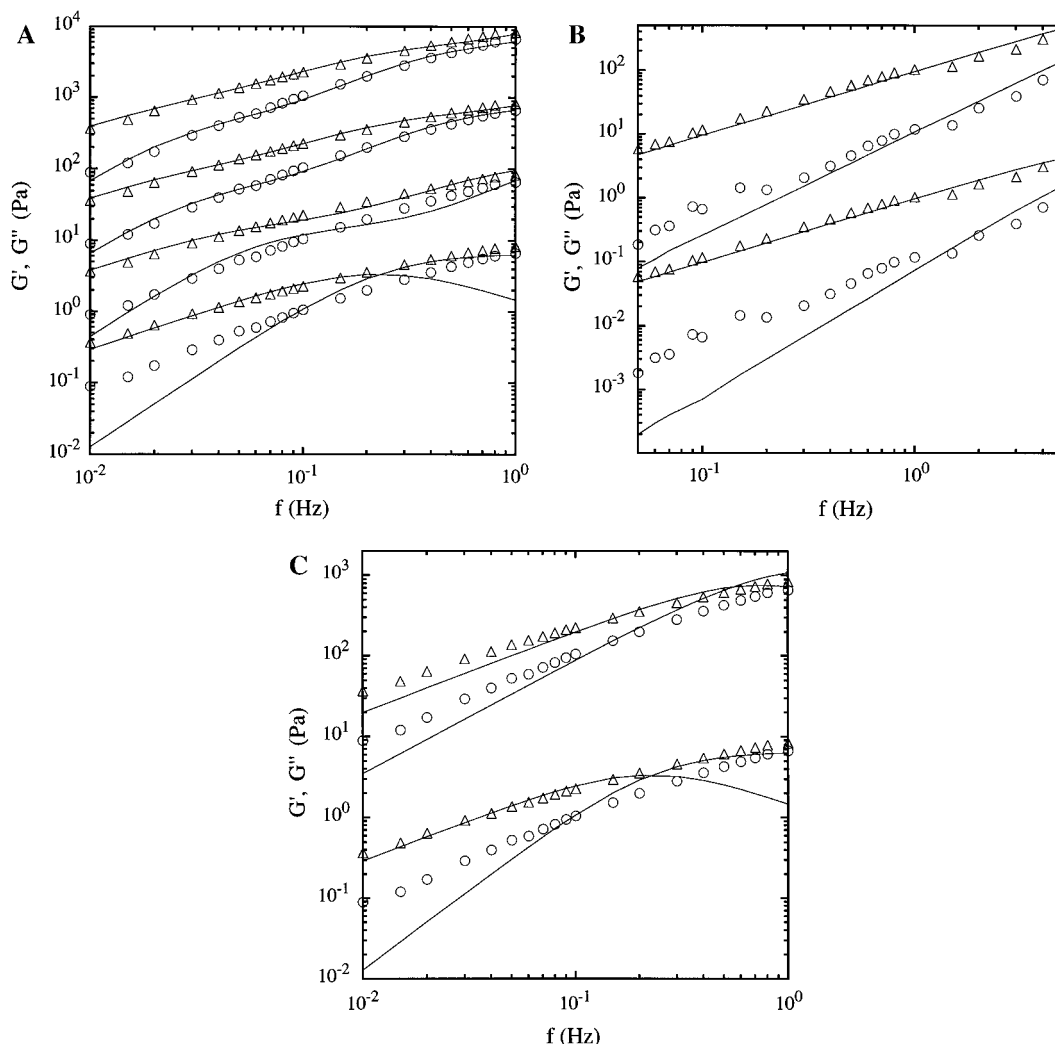
$$c_{s,max} = \beta_{max} c_h + \gamma_{max} cmc_s \quad (8)$$

where  $\beta_{max} = c_{s,b}/c_h$  is the ratio between surfactant  $c_{s,b}$  and polymer hydrophobic tails,  $c_h$ , in the mixed micelle.

Below, where eq 8 will be used to describe data from various HM-EHEC/surfactant mixtures, all polymer hydrophobic tails are assumed to be in the associated state (in a 1 w/w% HM-EHEC solution this corresponds to  $c_h = 0.64$  mm, see Materials section).

**Influence of SDS on Rheological Parameters.** The results in this paper will be presented in terms of the complex viscosity at a low frequency of 0.1 Hz,  $\eta_{0.1Hz}^*$ , (the same features as reported here are also observed at other low frequencies)

$$\eta^* = \frac{(G'^2 + G''^2)^{1/2}}{\omega} \quad (9)$$



**Figure 3.** (a) The frequency dependencies of  $G'$  (○) and  $G''$  (△) for a HM-EHEC solution with 2 mM SDS at 25 °C, have been fitted to a sum of Maxwell elements (full lines). From bottom to top there are, one, two, three, and four relaxation times. The three  $G'$  and  $G''$  curves at the top in the figure have been shifted vertically by multiplication with 10, 100, and 1000, respectively. (b)  $G'$  (○) and  $G''$  (△) as a function of frequency for a EHEC solution with 12.9 mM SDS at 25 °C have been fitted to a Maxwell model, lower curves, and to the modified Maxwell model according to eqs 5 and 6.  $G_\infty$  and  $e$  have been fixed at the values obtained from the fit of the same data to eq 7, upper curves. The upper curves have been shifted vertically by multiplication with 100. (c)  $G'$  (○) and  $G''$  (△) as a function of frequency for a HM-EHEC solution with 2 mM SDS at 25 °C have been fitted to a Maxwell model, lower curves, and to the modified Maxwell model according to eqs 5 and 6.  $G_\infty$  and  $e$  have been fixed at the values obtained from the fit of the same data to eq 7, upper curves. The upper curves have been shifted vertically by multiplication with 100.

and the time  $\tau_{\text{exp}}$  corresponding to the frequency of intersection  $f_c$  where  $G'$  equals  $G''$

$$\tau_{\text{exp}} = \frac{1}{2\pi f_c} \quad (10)$$

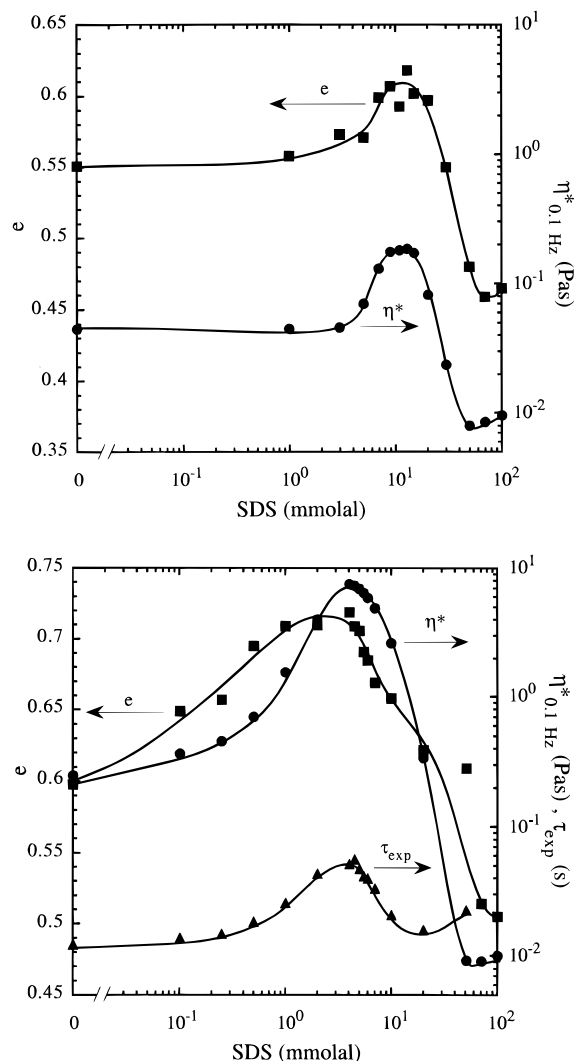
It is obvious from Figure 4 that the value of  $e$  starts to increase from a very low SDS concentration for the 1 w/w% HM-EHEC system, while for the 1 w/w% EHEC system the increase commences at a much higher SDS concentration. The same tendency is observed for the complex viscosity. These variations with the concentration of SDS, for  $e$  and the dynamic viscosity, have been pointed out in an earlier publication on the rheological behavior of EHEC and HM-EHEC.<sup>8</sup>

As has been concluded from phase separation studies,<sup>18</sup> rheology,<sup>8</sup> and binding experiments,<sup>19,17</sup> SDS associates to the EHEC chains. The increase in  $e$  and  $\eta_{0.1\text{Hz}}^*$  observed in Figure 4a can, thus, be assigned to enhanced polymer/surfactant interaction at moderate surfactant concentrations. At high SDS concentrations, the connectivity of the network is gradually lost<sup>15</sup> and the value of  $e$  approaches 0.5 (the value of a single Maxwell element) and  $\eta_{0.1\text{Hz}}^*$  decreases.

When it comes to the difference in behavior between the systems EHEC/SDS and HM-EHEC/SDS, this behavioral

difference can probably be rationalized in the following way. In the case of HM-EHEC/SDS it has been established that SDS binds to the polymer at a very low surfactant concentration, while for EHEC/SDS the binding starts at a higher SDS concentration.<sup>17</sup> A further consequence of this binding effect is that the maxima of  $e$  and  $\eta_{0.1\text{Hz}}^*$  for the two systems are located at different concentrations. (At increasing surfactant concentration the effect of the polymer hydrophobic tails, which are present in a low number, is expected to gradually decrease, and therefore the interaction between surfactants and the backbone of HM-EHEC is expected to approach that in the EHEC system. However, the effect correlated to this association is hidden by the much stronger effects induced by the binding to the polymer hydrophobic tails.)

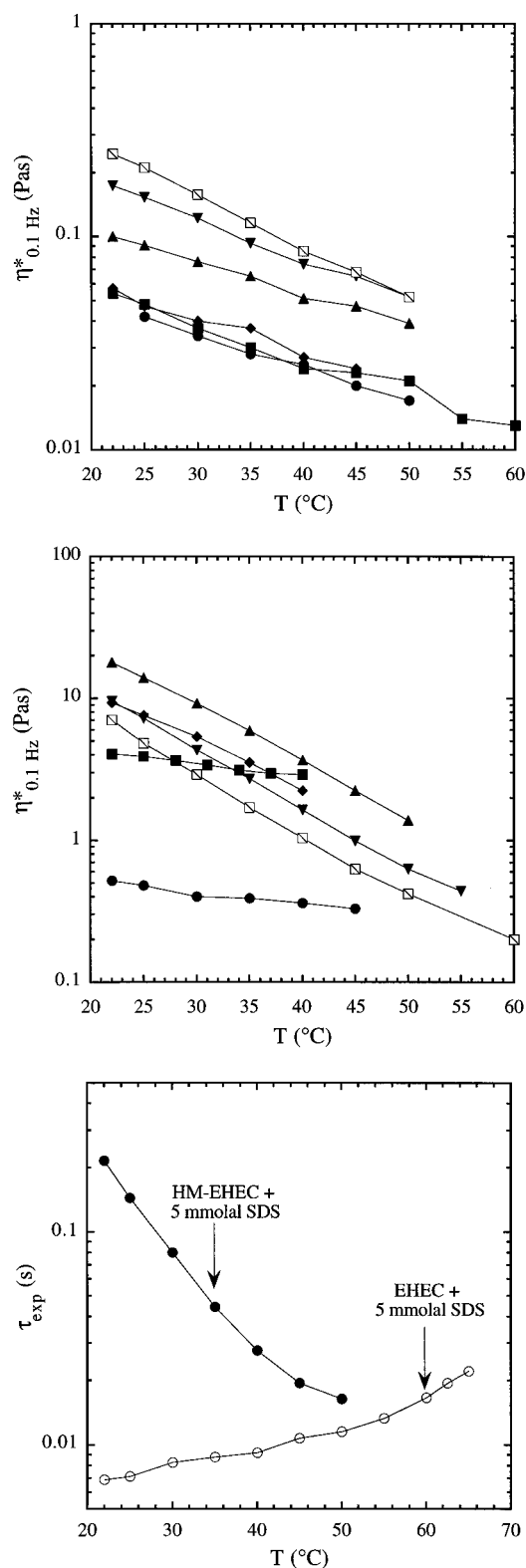
The influence of SDS on the intersection time  $\tau_{\text{exp}}$  for HM-EHEC is illustrated in Figure 4b. The increase of  $\tau_{\text{exp}}$  is due to enhanced hydrophobic interactions at moderate surfactant concentrations. The subsequent decrease is due to a weakening of the connectivity of the network at high SDS addition. In the case of EHEC/SDS  $\tau_{\text{exp}}$  has not been determined because it is too short to provide reliable results with the present rheometer (for EHEC,  $f_c$  is only reached at temperatures above room temperature, see below).



**Figure 4.** (a) Rheological parameters as a function of SDS addition for a 1 w/w% EHEC solution at 25 °C:  $\eta^*_{0.1 \text{ Hz}}$  (●) and  $e$  (■). The lines are only drawn as guidance for the eye. (b) Rheological parameters as a function of SDS addition for a 1 w/w% HM-EHEC solution at 25 °C:  $\eta^*_{0.1 \text{ Hz}}$  (●),  $e$  (■),  $G_\infty$ , and  $\tau_{\text{exp}}$  (▲). The lines are only drawn as guidance for the eye.

**The Effect of Temperature on Rheological Parameters in the (HM-)EHEC/SDS Mixtures.** Figure 5a,b show that  $\eta^*_{0.1 \text{ Hz}}$  decreases with increasing temperature for both EHEC and HM-EHEC at all SDS concentrations. This is a normal temperature dependence frequently observed for polymers as indicated by the following equation:  $\eta_0 \cong G_\infty \tau$ , where  $\eta_0$  is the viscosity at the Newtonian plateau and  $\tau$  is a characteristic relaxation time.<sup>20</sup> Provided that the topology of the system is not altered in the investigated temperature range, the plateau modulus  $G_\infty \cong nkT$  ( $n$  is the number of elastic active chains) should only exhibit a weak temperature dependence.<sup>21</sup>

Figure 5c shows the expected temperature dependence of  $\tau_{\text{exp}}$  for the HM-EHEC/5 mm SDS system, whereas  $\tau_{\text{exp}}$  displays a reversed temperature dependence for the EHEC/5 mm SDS system. Due to experimental limitations of the rheometer,  $f_c$  has only been determined for some EHEC/SDS mixtures. However,  $\tau_{\text{exp}}$  has been evaluated by extrapolation at low temperatures for the EHEC solution with 5 mm SDS. The extrapolation was made by linear extrapolations of  $G'$  and  $G''$  as a function of frequency (in a log–log plot). At higher temperatures,  $f_c$  was indeed in the experimental range of the rheometer, and  $\tau_{\text{exp}}$  increases with increasing temperature (see Figure 5c). The observed tendency for the EHEC polymer can be explained in the following way. As was discussed above, some parts of the polymer becomes more hydrophobic than



**Figure 5.** (a) The parameter  $\eta^*_{0.1 \text{ Hz}}$  as a function of temperature for EHEC/SDS mixtures: 0 mm SDS (●), 1 mm SDS (■), 3 mm SDS (◆), 5 mm SDS (▲), 7.5 mm SDS (▼), and 10 mm SDS (slanted □). The slightly different numerical values as compared to Figure 4a originate from different batches of the polymer from the purification procedure. (b) The parameter  $\eta^*_{0.1 \text{ Hz}}$  as a function of temperature for HM-EHEC/SDS mixtures: 0 mm SDS (●), 1 mm SDS (■), 3 mm SDS (◆), 5 mm SDS (▲), 7.5 mm SDS (▼), and 10 mm SDS (slanted □). The slightly different numerical values as compared to Figure 4b originate from different batches of the polymer from the purification procedure. (c)  $\tau_{\text{exp}}$  as a function of temperature for EHEC/5 mm SDS (○) and for HM-EHEC/5 mm SDS (●). The slightly different numerical values as compared to Figure 4b originate from different batches of the polymer from the purification procedure.

others upon an increased temperature, and this effect of enhanced hydrophobic associations may give rise to an increase of  $\tau_{\text{exp}}$  with increasing temperature. In this context we should note that dynamic light scattering measurements on a thermo-reversible gelling EHEC with a certain amount of surfactant showed that the characteristic time of the slow relaxation mode increased as a function of temperature. This effect, consistent with that observed for  $\tau_{\text{exp}}$ , has been attributed to a slowing down of the motions of the individual chains at higher temperature.<sup>12,13</sup>

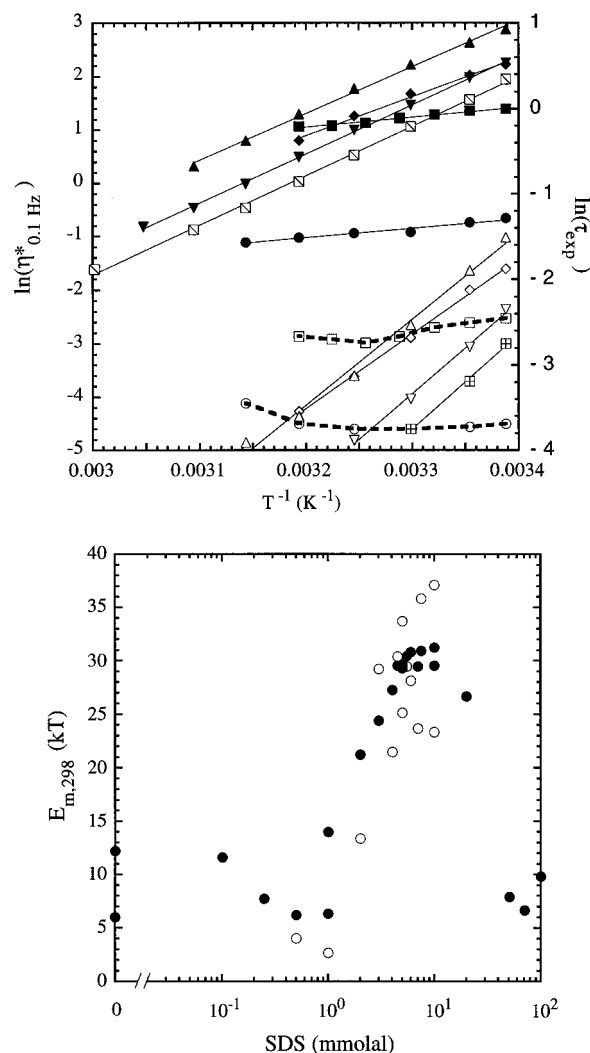
The hydrophobic associations between the hydrophobic tails of HM-EHEC are expected to slow down the motions of the polymer chains, and it can be seen in Figure 5c that  $\tau_{\text{exp}}$  is much longer for the HM-EHEC/SDS system than for the EHEC/SDS system at a given low temperature. This trend can be anticipated since the hydrophobic association for the HM-polymer at a moderate surfactant concentration is much stronger than that for the unmodified analogue. The temperature dependence of  $\tau_{\text{exp}}$  for the HM-EHEC/5 mM SDS system (see Figure 5c) can probably be rationalized in the following way. The hydrophobicity of the polymer hydrophobic tails is not expected to increase with increasing temperature. Therefore the observed decrease of  $\tau_{\text{exp}}$  with increasing temperature is not surprising, and the temperature dependence of  $\tau_{\text{exp}}$  may follow the Arrhenius behavior.

$$\tau_{\text{exp}} \propto e^{E_m/kT} \quad (11)$$

The activation energy  $E_m$  is related to the difference in free energy of the process of transferring a hydrophobic tail from the mixed micelle to an aqueous environment. However, we should note that  $E_m$  also consists of contributions from polymer kinetics.

In Figure 6a an Arrhenius plot for the HM-EHEC system at various SDS concentrations is depicted. The corresponding activation energies are determined from the slopes of the lines and the values are given as a function of SDS concentration in Figure 6b. Satisfactory fits were obtained except at low SDS concentrations (0 and 1 mM). At the present we do not know why  $\tau_{\text{exp}}$  has a different temperature dependence at low SDS concentrations, but this effect and the scatter in the points may originate from the temperature dependence of the parent EHEC molecules, together with an uncertainty in the determinations of  $f_c$ , especially at high temperatures, because this frequency was on the limit of the performance of the rheometer. Values of  $E_m$  as a function of SDS have also been determined from  $\eta_{0.1\text{Hz}}^*$  and they are in agreement, within experimental errors, with those calculated from  $\tau_{\text{exp}}$ . This indicates that the number of active elastically chains are independent of the temperature in the investigated temperature regime. Despite scatter in the points, the result in Figure 6b suggests that the activation energy passes through a maximum similar to that observed for the complex viscosity (see Figure 4b). The increase in  $E_m$  indicates that the binding of surfactant molecules to the polymer and the formation of mixed micelles is accompanied by a decreased free energy of the polymer hydrophobic tails in the bound state. At high SDS concentrations, the contribution to  $E_m$  from the polymer hydrophobic tails vanishes as the connectivity given by mixed micelles between these tails and SDS molecules is gradually lost.

We conclude that the difference between the two polymer systems is that with HM-EHEC it is the hydrophobic tails that preferentially interact with the surfactant, while with EHEC it is the hydrophobic parts of the polymer backbone itself that interact. Furthermore, the hydrophobic interactions are favored at elevated temperature for EHEC, while for the HM-EHEC

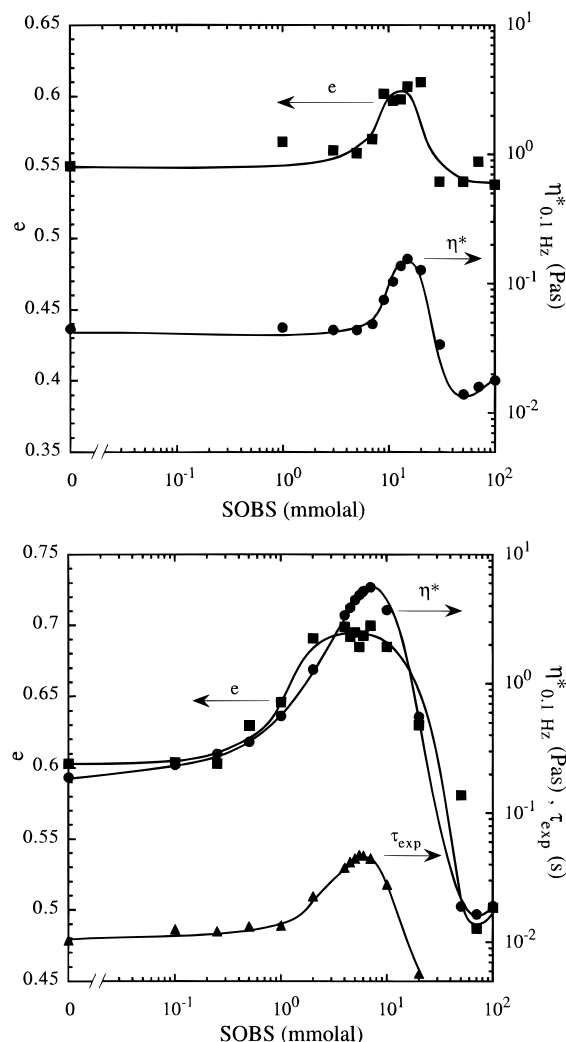


**Figure 6.** (a) An Arrhenius plot of  $\ln(\eta_{0.1\text{Hz}}^*)$  and  $\ln(\tau_{\text{exp}})$  as a function of  $1/T$  for HM-EHEC/SDS mixtures: 0 mM SDS (●, ○), 1 mM SDS (■, □), 3 mM SDS (◆, ◇), 5 mM SDS (▲, △), 7.5 mM SDS (▼, ▽) and 10 mM SDS (slanted □) for  $\ln(\eta_{0.1\text{Hz}}^*)$  and  $\ln(\tau_{\text{exp}})$ , respectively. Full lines represent best fits to straight lines, while dashed lines are only drawn as guidance for the eye. (b) The activation energy  $E_m$  (see text) for HM-EHEC/SDS mixtures.  $E_m$  was evaluated from  $\tau_{\text{exp}}$  (○) and from  $\eta_{0.1\text{Hz}}^*$  (●).

polymer the temperature has no significant impact on the hydrophobic association situation.

**Influence of Different Surfactants on Rheological Properties.** The modulation of rheological parameters on addition of other surfactants than SDS has only been investigated at one temperature (25 °C). The knowledge gained from the addition of SDS to the polymer solutions will be used in the interpretation of the results below. We start by the addition of the anionic surfactant SOBS to EHEC and HM-EHEC (Figure 7). It can be seen that the effects of SOBS is closely related to those seen in the presence of SDS. The effect of the bulky head group and of the different structure of the hydrophobic tail of the surfactant seems to be moderate, but can possibly be seen in the slightly lower numerical values of  $\eta_{0.1\text{Hz}}^*$  and  $\tau_{\text{exp}}$  at their respective maxima (see Table 2). Furthermore, the  $c_{\text{cac}}$  for the EHEC/SOBS mixture, and therefore  $c_{\text{s,max}}$  (see Table 3) for the HM-EHEC/SOBS mixture, is higher for SOBS than for SDS (see below). These results indicate that the interaction between polymer and surfactant is slightly weaker with SOBS than in the presence of SDS.

In Figures 8–10 the effects of addition of C<sub>12</sub>TAC, C<sub>16</sub>TAC, and C<sub>18</sub>TAC to EHEC and HM-EHEC solutions are depicted. Basically, the main features seem to be the same as those on



**Figure 7.** (a) Rheological parameters  $\eta^*_{0.1\text{Hz}}$  (●) and  $e$  (■) in the presence of SOBS for a 1 w/w% EHEC solution at 25 °C. The lines are only drawn as guidance for the eye. (b) Rheological parameters  $\eta^*_{0.1\text{Hz}}$  (●),  $e$  (■), and  $\tau_{exp}$  (▲) in the presence of SOBS for a 1 w/w% HM-EHEC solution at 25 °C. The lines are only drawn as guidance for the eye.

addition of SDS, and we will focus our attention on the differences between the systems. The cationic surfactants have generally a weaker interaction with EHEC than the anionic SDS. This can especially be seen in the numerical values of  $\eta^*_{0.1\text{Hz}}$  (see Table 2). This is in line with the general opinion that the interaction between a nonionic polymer and a cationic surfactant is weaker than with a corresponding anionic surfactant.<sup>22</sup> For HM-EHEC, the surfactant chain length has to be increased to 18 carbons for cationic surfactants to have a viscosity increase and a characteristic time,  $\tau_{exp}$ , comparable to that with the anionic SDS. Thus, also the interaction between surfactants and the polymer hydrophobic tails seems to be weaker with

**TABLE 3:  $\text{cmc}_s$  Values are Extracted from the Phase Behavior of EHEC, As the Surfactant Concentration where the Phase Separation Temperature Starts to Increase<sup>a</sup>**

surfactant	$\text{cmc}_s$ (mM)	$c_{s,\text{max}}$ (mM)	$c_{s,\text{dis}}$ (mM)	$N_{\text{agg}}$
SDS	3.2	4.5	50	73
SOBS	5.2 <sup>b</sup>	6.9	50	70
C <sub>12</sub> TAC	19	20.6	52	52
C <sub>16</sub> TAC	0.5	5.4 <sup>c</sup>	52	80
C <sub>18</sub> TAC	0.2	4.7 <sup>c</sup>	71	111
C <sub>12</sub> E <sub>8</sub>	0.07 <sup>d</sup>	1	20	31

<sup>a</sup> From ref 18. <sup>b</sup> The  $\text{cmc}_s$  value for SOBS was extracted from viscosity as the surfactant concentration where  $\eta^*_{0.1\text{Hz}}$  starts to increase for EHEC (as no phase studies were made with this surfactant). <sup>c</sup>  $c_{s,\text{max}}$  value for C<sub>16</sub>TAC and C<sub>18</sub>TAC are recalculated by using eq 12 in combination with eq 8 before they were plotted in Figure 12. <sup>d</sup> C<sub>12</sub>E<sub>8</sub> showed no interaction with EHEC and the relevant  $\text{cmc}_s$  equals the cmc in the binary surfactant/water system.

cationic than with anionic surfactants. Possibly part of the explanation can be attributed to the same reasons that give higher  $\text{cmc}$ 's of cationic surfactants as compared to anionic of the same chain length (see Table 1).<sup>23,24</sup> These studies indicate that cationic surfactants in general have a weaker tendency to assemble in aggregates than their anionic analogues. Another difference is that, compared to anionic surfactants,  $\eta^*_{0.1\text{Hz}}$  attains higher values at high surfactant concentrations with cationic surfactants (for both EHEC and HM-EHEC systems). This can for instance be seen in Figure 9a which shows that  $\eta^*_{0.1\text{Hz}}$  does not decrease much after the maximum for the EHEC/C<sub>16</sub>TAC system. The C<sub>n</sub>TAC surfactants (and also SOBS) seem to be inferior to SDS in dissolving the "lumps" or cross-links between different polymer chains (see also Table 2).<sup>15</sup>

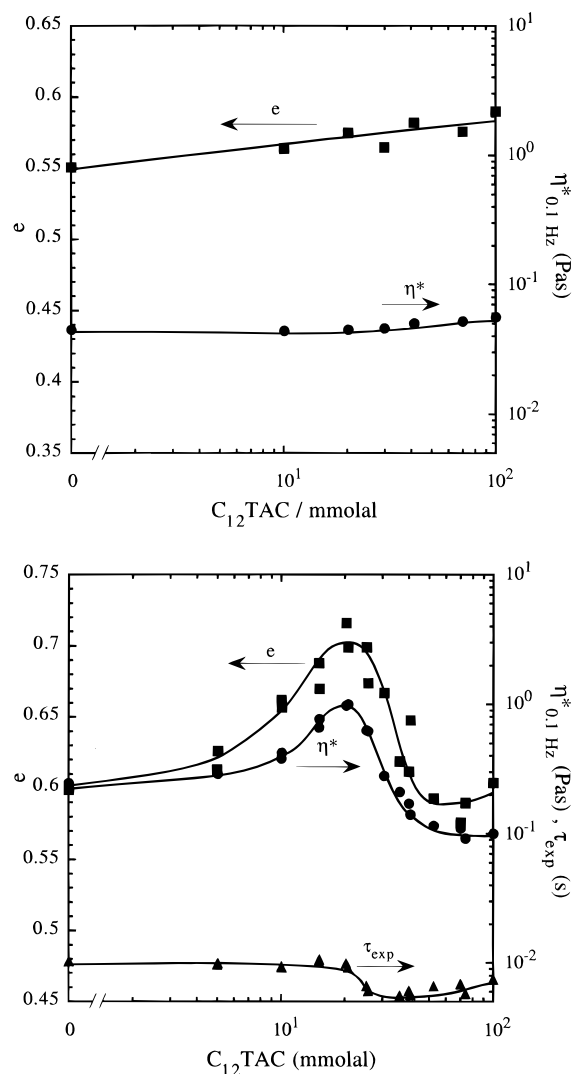
Figure 11 shows the effect of the addition of the nonionic surfactant C<sub>12</sub>E<sub>8</sub> on the rheological parameters of 1 w/w% aqueous solutions of EHEC and HM-EHEC. In the accompanying paper<sup>18</sup> it was shown that EHEC and C<sub>12</sub>E<sub>8</sub> do not associate, which is in line with the results in Figure 11a. For the HM-EHEC polymer, a weak association is seen initially and  $\eta^*_{0.1\text{Hz}}$  increases slightly. After the maximum, where the mixed micelles are expected to decrease the connectivity between different HM-EHEC chains, a decrease in  $\eta^*_{0.1\text{Hz}}$  is observed. The same pattern of behavior is seen in the characteristic time  $\tau_{exp}$ .

In Table 3 data of various HM-EHEC/surfactant mixtures are displayed. To be able to express these data in the framework of eq 8 we have to consider that all surfactants except C<sub>16</sub>TAC and C<sub>18</sub>TAC have hydrocarbon chains containing 12 carbons. The increase in surfactant chain length will result in an increased number of binding sites,<sup>18</sup> which will act to postpone the cooperative part of the binding process and hence, results in an increased  $c_{s,\text{max}}$ . This can also be seen from a comparison of Figures 8b, 9b, and 10b where a clear trend toward a wider viscosity maximum with surfactant chain length can be observed. The simplest way to account for the change in  $c_{s,\text{max}}$  with surfactant chain length is to correlate it to the alteration of

**TABLE 2: Approximate Numerical Values<sup>a</sup> of  $\eta^*_{0.1\text{Hz}}$  and  $\tau_{exp}$**

	$\eta^*_{\text{init}}$ EHEC	$\eta^*_{\text{init}}$ HM-EHEC	$\eta^*_{\text{max}}$ EHEC	$\eta^*_{\text{max}}$ HM-EHEC	$\eta^*_{\text{final}}$ EHEC	$\eta^*_{\text{final}}$ HM-EHEC	$\tau_{exp,\text{init}}$ HM-EHEC	$\tau_{exp,\text{max}}$ HM-EHEC	$\tau_{exp,\text{final}}$ HM-EHEC
SDS	0.045	0.25	0.19	7.4	0.008	0.008	0.012	0.052	0.015
SOBS	0.045	0.19	0.16	5.7	0.016	0.016	0.010	0.046	0.006
C <sub>12</sub> TAC	0.045	0.24	0.056	1.0		0.096	0.010	0.01	0.006
C <sub>16</sub> TAC	0.045	0.25	0.072	3.1	0.064	0.14	0.012	0.023	0.006
C <sub>18</sub> TAC	0.045	0.19	0.10	9.2	0.053	0.10	0.010	0.052	0.008
C <sub>12</sub> E <sub>8</sub>	0.045	0.19		0.28		0.074	0.010	0.011	0.006

<sup>a</sup> Values without any surfactant added, at the surfactant concentration where the parameter is at maximum and at a high surfactant concentration (where many of the parameters have decreased substantially from the values determined at their maxima). The slightly different initial numerical values of the rheological parameters are due to different batches from the purification procedure.



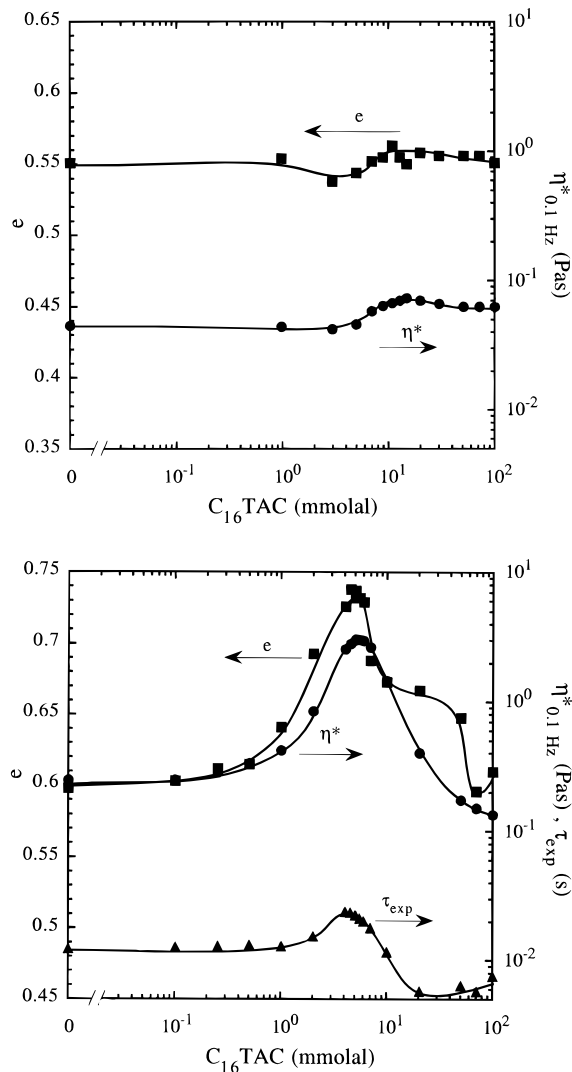
**Figure 8.** (a) Rheological parameters  $\eta_{0.1\text{Hz}}^*$  (●) and  $e$  (■) in the presence of  $\text{C}_{12}\text{TAC}$  for a 1w/w% EHEC solution at 25 °C. The lines are only drawn as guidance for the eye. (b) Rheological parameters  $\eta_{0.1\text{Hz}}^*$  (●),  $e$  (■), and  $\tau_{\text{exp}}$  (▲) in the presence of  $\text{C}_{12}\text{TAC}$  for a 1w/w% HM-EHEC solution at 25 °C. The lines are only drawn as guidance for the eye.

the micellar aggregation number by a changed volume of the micellar hydrocarbon core as follows from the increased chain length. The change in aggregation number  $N$  by an increased hydrocarbon chain length can be expressed as

$$\frac{N_1}{N_2} \cong \left( \frac{n_1}{n_2} \right)^2 \quad (12)$$

where  $n$  represents the number of carbons in the surfactant tail. In Figure 12, the data in Table 3 have been plotted and  $\beta_{\text{max}}$  is determined to 2.8 and  $\gamma_{\text{max}}$  to 1.0 by fitting a straight line to the data points and by making an identification with eq 8. These values agree with those found for other hydrophobically modified polymers,<sup>16</sup> in spite of the uncertainties in the data introduced when determining  $\text{cmc}_s$  and  $c_{s,\text{max}}$ .

In Table 3 is also given the point  $c_{s,\text{dis}}$  at high surfactant concentrations where the viscosity attains a constant value, and all interpolymer bonds can be assumed to be broken. From eq 13 an apparent aggregation number to induce a complete connectivity loss can be calculated, by assuming that each polymer hydrophobic tail has one, and only one, associated micelle,  $N_{\text{agg}} = c_{s,\text{b}}/c_{\text{h}}$ . (Of course this only gives a rough estimate. The polymer hydrophobic tails can, for instance, be



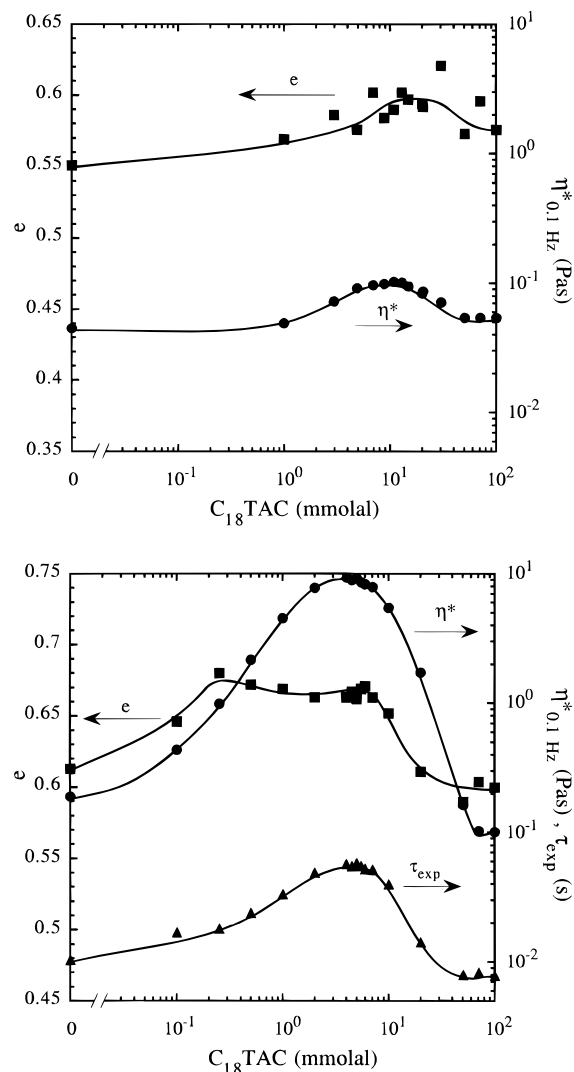
**Figure 9.** (a) Rheological parameters  $\eta_{0.1\text{Hz}}^*$  (●) and  $e$  (■) in the presence of  $\text{C}_{16}\text{TAC}$  for a 1w/w% EHEC solution at 25 °C. The lines are only drawn as guidance for the eye. (b) Rheological parameters  $\eta_{0.1\text{Hz}}^*$  (●),  $e$  (■), and  $\tau_{\text{exp}}$  (▲) in the presence of  $\text{C}_{16}\text{TAC}$  for a 1w/w% HM-EHEC solution at 25 °C. The lines are only drawn as guidance for the eye.

distributed in blocks along the polymer chain, which implies that two or more hydrophobic tails can reside in the same micelle without connecting different polymer chains.)

$$c_{s,\text{dis}} \approx \beta_{\text{dis}} c_{\text{h}} + \text{cmc}_s \quad (13)$$

Interestingly,  $N_{\text{agg}}$  for  $\text{C}_{12}\text{E}_8$ , which has been concluded not to associate with the EHEC molecule,<sup>18</sup> is in accordance with aggregation numbers found for a hydrophobically modified hydroxyethyl cellulose (HM-HEC).<sup>16</sup> The parent polymer in that system, HEC, does not bind to surfactant micelles.<sup>25</sup>  $N_{\text{agg}}$  for SDS and SOBS are comparable (ca. 70), and disagrees with the aggregation number determined from fluorescence quenching (ca. 46 at a total SDS concentration of 40 mM).<sup>17</sup> The difference in these numbers most likely has its origin from the surfactant interaction with the polymer backbone. A calculation based on the assumption that polymer bound micelles only interact with polymer hydrophobic tails gives a calculated  $N_{\text{agg}}$  that is too large, as the number of polymer bound micelles increases due to the interaction with other parts of the polymer molecules. The same explanation accounts for  $N_{\text{agg}}$  in the  $\text{C}_{12}\text{TAC}$  system (ca. 52), which is lower than that for SDS but higher than that for  $\text{C}_{12}\text{E}_8$ . The intermediate aggregation number can be expected as the interaction of  $\text{C}_{12}\text{TAC}$  with EHEC is weaker





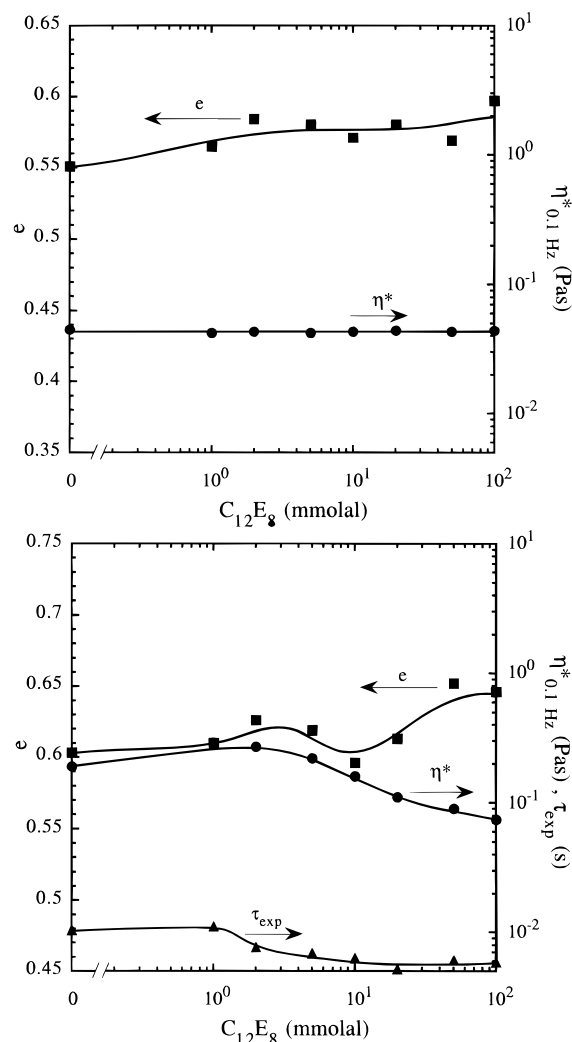
**Figure 10.** (a) Rheological parameters  $\eta_{0.1\text{ Hz}}^*$  (●) and *e* (■) in the presence of C<sub>18</sub>TAC for a 1w/w% EHEC solution at 25 °C. The lines are only drawn as guidance for the eye. (b) Rheological parameters  $\eta_{0.1\text{ Hz}}^*$  (●), *e* (■), and  $\tau_{\text{exp}}$  (▲) in the presence of C<sub>18</sub>TAC for a 1w/w% HM-EHEC solution at 25 °C. The lines are only drawn as guidance for the eye.

than the interaction of SDS with EHEC, but stronger than the interaction seen with C<sub>12</sub>E<sub>8</sub>. The higher  $N_{\text{agg}}$  for both C<sub>16</sub>TAC and C<sub>18</sub>TAC probably results from a combination of an increased interaction with EHEC and from the trivial effect from an increased surfactant tail length.

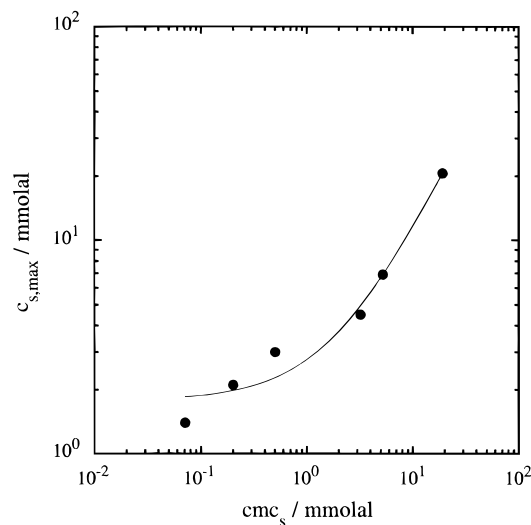
### Summary and Conclusions

It has been shown that evaluation of rheological measurements in a simple model can give essential qualitative information about the polymer/surfactant interaction and aggregation. We have drawn attention to differences but also to similarities between the EHEC and HM-EHEC systems. Similarities exist as the EHEC molecule itself contains both hydrophilic and hydrophobic parts, and presumably the difference in hydrophobicity between these parts increases at higher temperatures as the polymer becomes progressively more hydrophobic. For EHEC polymers in the presence of an ionic surfactant, the polyelectrolyte and hydrophobic effects are discussed in the framework of a model developed by Cabane et al. In this model the interplay between swelling of the network (caused by the ionic surfactant) and connectivity (established by “lumps” or hydrophobic associations) is considered.

A simple approach, based on a modified Maxwell model, accounts for the low-frequency behavior and a pseudo plateau



**Figure 11.** (a) Rheological parameters  $\eta_{0.1\text{ Hz}}^*$  (●) and *e* (■) in the presence of C<sub>12</sub>E<sub>8</sub> for a 1w/w% EHEC solution at 25 °C. The lines are only drawn as guidance for the eye. (b) Rheological parameters  $\eta_{0.1\text{ Hz}}^*$  (●), *e* (■), and  $\tau_{\text{exp}}$  (▲) in the presence of C<sub>12</sub>E<sub>8</sub> for a 1w/w% HM-EHEC solution at 25 °C. The lines are only drawn as guidance for the eye.



**Figure 12.**  $c_{s,\text{max}}$  as function of  $\text{cmc}_s$  (see text). The curve describes the best linear fit of the data points to eq 8.

value in the storage modulus associated with the relaxation times important in this frequency window of the mechanical spectra can be extracted. The scaling exponent *e* gives an indication of the number of relaxation modes in the investigated frequency

regime and their relative strengths. A high value of  $e$  suggests a broad distribution of relaxation times which are only partly separated. As an illustration of difficulties in drawing any final conclusions from the value of the exponent  $e$  we refer to Figure 9a. It can be seen that  $\eta_{0.1\text{Hz}}^*$  follows the trend that indicates that the surfactant associates to the polymers, while the result of  $e$  is not conclusive.

The rheological results revealed significant polymer/surfactant interaction for EHEC and HM-EHEC in the presence of an ionic surfactant. The rheological parameters displayed an interaction peak for both EHEC and HM-EHEC, but the maximum of the peak was located at a lower surfactant concentration for the hydrophobically modified polymer than for the unmodified analogue. The interaction peak was much less pronounced when a nonionic surfactant was used.

An investigation of the temperature dependence revealed that the value of characteristic time  $\tau_{\text{exp}}$  of HM-EHEC was determined by the level of association of polymer hydrophobic tails and surfactant molecules into mixed micelles. The unmodified EHEC exhibited a reversed temperature dependence of the characteristic time, indicating that the relaxation process is slowed down due to enhanced hydrophobic associations at higher temperatures. This is a well-known feature of certain EHEC samples that show a temperature-induced gel formation. Although, the present EHEC sample does not form a gel at elevated temperature, the hydrophobic associations are strengthened considerably with increasing temperature.

In the final part of the paper, dealing with the interactions of different surfactants with the polymers, it was shown that the HM-EHEC polymer displays a general pattern of behavior (in analogy with other nonionic as well as ionic HM-polymers) in the formation and breakdown of the network formed by polymer/surfactant associations. We also found that the width of the viscosity maximum with surfactant concentration increases as the surfactant chain length increases. This observation was referred to an increased surfactant aggregation number in the mixed micelles, which postpones the cooperative part of the binding process, and, therefore, the breakdown of the polymer/surfactant network. The recognition should be important in applications where the main purpose of addition of a hydrophobically modified polymer is to control the rheology.

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