The interaction between water-soluble polymers and surfactant aggregates

Brackman, Josephine Charlotte

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CHAPTER 3

THE INFLUENCE OF POLYMERS ON THE MICELLIZATION OF
CETYLTRIMETHYLLAMMONIUM SALTS

3.1 Introduction

3.1.1 Cetyltrimethylammonium salts

Cetyltrimethylammonium salts (CTAX), particularly the bromide and chloride, are by far the most widely studied cationic surfactants. Although this one-sided interest probably stems from their easy availability, they are indeed interesting surfactants. The formation of viscoelastic solutions at extremely low concentrations (ca. $10^{-4}$ M) in the presence of salicylate anions\textsuperscript{119} is an especially fascinating phenomenon. Notwithstanding these interesting properties, CTAX salts as well as the relatively few other cationic surfactants that have been investigated, have a poor reputation in the field of polymer-micelle chemistry\textsuperscript{3}. This stems from the fact that they give only significant interaction with rather hydrophobic polymers, though recently a modest propensity for binding to more hydrophilic polymers has been detected\textsuperscript{120-122}.

After a brief overview on CTAX/polymer interaction and on the formation of rodlike micelles in the presence of specific counterions, this chapter will deal with the interaction of micelles of CTAB ($X =$ bromide), CTATs ($X =$ tosylate), and CTASal ($X =$ salicylate) with polymers. The relatively hydrophobic polymers PVME and PPO both induce a decrease in aggregation number of CTAB and an increase in the concentration at which the transition from spherical to rodlike micelles takes place for CTATs. These findings support the view that the disappearance of the gel-like and viscoelastic properties of a CTASal solution in the presence of PVME or PPO originate from a preferential binding of the polymers to spherical micelles.
rather than to rodlike micelles.

3.1.2 Interaction of polymers with cationic surfactants

The early work of Saito\(^4\) already revealed that the cationic surfactants \(n\)-dodecylammonium chloride (DAC), \(n\)-dodecyl- and stearyltrimethylammonium chloride (DTAC and STAC) and 1-cetylpyridinium chloride do not interact with PVP, PVA, and PEO. Saito\(^4\) was also the first to suggest that the large size of the trimethylammonium headgroup might be the cause. This explanation does not hold, however, for DAC. Furthermore he found that the hydrophobic polymer PPO (mw 2,000) does interact with DTAC and DAC.

Several other authors also allude to the fact that the interaction of polymers with micelles formed from anionic surfactants is much more facile than with micelles composed of cationic surfactants\(^3,8,5,6,7,1,8,0,1,2,3,1,2,4\). The criteria used to establish the absence of interaction between micelles of cationic surfactants and hydrophilic polymers include viscometry of PEO\(^6,1,8\) and PVP\(^4\) solutions, the study of thermodynamic quantities\(^5,8\), fluorescence probe measurements\(^5,3\), and solubilization experiments\(^4,8\).

Recently, however, potentiometric studies with ion (surfactant) selective electrodes by Shirahama\(^1,2,2,1,2,5\) and others\(^7,8\) have revealed a feeble and virtually non-cooperative interaction of CTAB with PVA and PEO\(^8\). There are no indications for binding to PVP. Furthermore, Perron et al.\(^5,8\) found a slight influence of PEO, but not of PVP, on the heat capacity of a CTAB solution. Since cooperativity of the binding process is almost absent, it has been suggested that surfactant monomers bind to the macromolecule\(^7,8,1,2,2,1,2,5\). Anyway, the interaction is about a hundred times weaker than with SDS. The cooperativity and the amount of binding of cationic surfactants to PVA is greatly enhanced when the hydrophobicity of the macromolecule is increased by acetylation (up to 12%)\(^7,8,1,2,5\). This is in accord with the finding that hydrophobic polymers\(^1,2,4\) like PPO\(^4,6,5,6,7,6,8\), HPC\(^5,3\) and ethylhydroxyethylcellulose (EHEC)\(^7,8,0\) interact with cationics similarly to SDS.
Interaction with cationic surfactants is also promoted by the presence of a strongly interacting counterion such as SCN−. Saito and coworkers55 found that DA+SCN−, as judged by reduced viscosity data, interacts quite strongly with PVA-Ac (with 30% acetate residues) and PVP whereas the corresponding chloride shows comparatively weak interactions. Regrettably, this line of studies has not been continued.

Three explanations have been advanced for the origin of the weakness of the interactions between polymers and cationic surfactants: (i) the bulkiness of the cationic headgroup, (ii) a positive charge (vide infra) on the polymer, and (iii) a difference in interaction of cations and anions with the hydration sheath of the polymer. The first explanation, which is the oldest and still the most popular one, has been proposed by Saito4, and has later been adopted by Nagarajan61. The bulkiness of the headgroup of most cationic (and nonionic) surfactants is assumed to hamper the presence of a polymer at the hydrocarbon-water interface. Furthermore, a bulky headgroup quite effectively shields the hydrophobic core. Thus, the stabilization of the core-water interface by the polymer is less relevant in that case than in case of micelles of which the core is less shielded by the headgroups. Small angle neutron scattering studies indeed reveal that the trimethylammonium headgroup in micelles of n-tetradecyltrimethylammonium bromide does not even leave enough space for penetration of water molecules between the headgroups126,127. An opposite situation applies for sulfate surfactants, where extensive core-water contact is suggested by NMR and small-angle neutron scattering measurements128. Ruckenstein71 suggests a more indirect interaction, but also considers the bulkiness to be critical. There are, however, several observations which cannot be reconciled with the bulkiness playing a major role. These include: (i) DAC and protonated n-dodecyltrimethylamineoxide (DDAOH+) micelles (Chapter 4) do not interact with PEO, PVP, and PVA or only very weakly and (ii) the finding that the bulkiness of the hydrophobic polymers does not prevent interaction with, for instance, CTAB, having a voluminous trimethylammonium headgroup.

The second explanation8,123 involves electrostatic repulsion with a proposed slightly positive charge on the polymers. This charge is thought to
originate from protonation of the ether oxygens in the case of polyethers and the amide moiety in the case of PVP. The pH dependence of the interaction between SDS and PEO was used by Schwuger\textsuperscript{8} to support this view. Moroi and Saito\textsuperscript{123} used the same concept to explain the difference between DTAB and SDS in mixed micelle formation with nonionic micelles of the poly(oxyethylene)alkylether type. The very low pK\textsubscript{a} value of an ether or amide (pK\textsubscript{a} (CH\textsubscript{3}CONH\textsubscript{2})H\textsuperscript{+} = 0.3), however, raises serious doubts about the importance of protonation at neutral pH.

The third explanation is based on the different influence of cations and anions on the hydration sheath of the polymer, and thus of headgroup-polymer interaction. To support this view Witte\textsuperscript{65} refers to the work of Napper\textsuperscript{129}, who studied the role of electrolytes in the flocculation behavior of polymers. The decrease in clouding temperature of PEO by the addition of salts also indicates the more pronounced influence of anions compared to cations\textsuperscript{42,48,50,130}. Ataman\textsuperscript{50} stated that "the suppression of the cloud point temperature of PEO ..., appears to be a combined cation/anion effect, but the anion effect seems predominant". It is noteworthy that the sulfate ion belongs to the more effective anions, whereas for instance NH\textsubscript{4}\textsuperscript{+} is one of the least effective cations\textsuperscript{50}. The ion-polymer interactions are usually thought to occur via hydration shell overlap effects.

Probably the size of the headgroup and the interaction of the headgroup with the hydration sheath of the polymer are the main reasons for weak interaction of cationic micelles with polymers. The electrostatic repulsion between polymer and micelles may modify interactions at low pH, but do not seem to be decisive under neutral conditions. Altogether, only an appreciably hydrophobic polymer can overcome these factors by a favorable free energy of transfer of polymer segments from the aqueous to the micellar phase and interact also with cationic (and nonionic) micelles.

3.1.3 Rodlike micelles of CTAX salts

So far, only the interaction of spherical cationic micelles with polymers
has been discussed. Certain cetyltrimethylammonium salts, however, are well known for the formation of rodlike micelles (Figure 3.1). For instance, for the salicylate salt, Hirata et al.\textsuperscript{132,133} even published electron micrographs of these rods, but these results have been criticized and are most likely artifacts associated with chemical staining. The use of cryo-transmission electron microscopy avoids these artifacts and direct imaging of the rods has become feasible\textsuperscript{134}. From these direct images of the rods, it appeared that the diameter (45 to 60 Å) is in agreement with expectations\textsuperscript{134}, contrary to the diameter of 100 to 120 Å reported by Hirata\textsuperscript{132}.

Surprisingly, Nagaragan\textsuperscript{61e} is the only author who considered rodlike micelles in the study of polymer-micelle interactions. He predicted theoretically that rodlike micelles of SDS formed in the presence of NaCl would be transformed to polymer-bound ellipsoidal micelles in the presence of PEO. Rodlike micelles of C\textsubscript{12}E\textsubscript{6} would be unaffected by PEO. However, Nagaragan did not publish or perform any experiments to test his predictions. Consequently, this section deals only with the structure and properties of rodlike micelles, of CTA\textsuperscript{+} in particular, in the absence of polymer.

The formation of rodlike micelles from CTA\textsuperscript{+} depends mainly on the structure and concentration of counterions\textsuperscript{135,136}. Whereas CTAB forms rodlike

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{rodlike_micelles.png}
\caption{Schematic representation of a network of rodlike micelles in a viscoelastic surfactant solution. Taken from ref. 131.}
\end{figure}
micelles only at high concentrations\textsuperscript{20a,137a,138,139}, CTAS\textsuperscript{131,140-142} produces viscoelastic solutions, indicating the presence of rods, even below 1 mM\textsuperscript{119}. Other hydrophobic counterions, such as \textit{m-} and \textit{p-}chlorobenzoate\textsuperscript{135}, tosylate\textsuperscript{137a}, benzenesulfonate\textsuperscript{137a}, naphthalenesulfonate\textsuperscript{143}, and \textit{o-}iodophenol\textsuperscript{133}, also induce rod formation, though not as effectively as salicylate. Interestingly, the precise substitution pattern of the aromatic ring of the counterion is of decisive importance\textsuperscript{135,136,138,144}. For instance, \textit{m-} and \textit{p-}hydroxybenzoate\textsuperscript{136,138,144} are no more effective than bromide, whereas the \textit{o-}isomer is very effective. On the other hand \textit{o-}chlorobenzoate is ineffective, but the \textit{p-} and \textit{m-}isomers are\textsuperscript{135,138}. Rao et al.\textsuperscript{135,145} revealed a correlation between the orientation of the counterion at the micellar surface and its rod-inducing efficiency. He suggested that the salicylate and \textit{m-}chlorobenzoate ions, which protrude from the micellar surface, serve as bridges between beads (Figure 3.2). However Anet\textsuperscript{146}, among others\textsuperscript{143,254}, disagrees with this view and argue in favor of the ‘rod’ model. The matter is still actively debated in the literature. At this moment ‘rods’ are still most

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{figure3_2.png}
\caption{Schematic representation of the orientation of (a) salicylate, and (b) \textit{m-}hydroxybenzoate molecules, embedded into a CTAB micelle, and (c) a chain of CTAB micelles linked through salicylate ions. Taken from ref. 145.}
\end{figure}
generally accepted, largely because the 'string'-model seems too elaborate as an explanation for such a common phenomenon as large aggregates producing viscoelastic solutions\textsuperscript{143}.

Apart from the question, whether 'strings' or 'rods' are present in CTASal solutions, the viscoelasticity at the extremely low concentrations remains a puzzle. Wennerström and Gravsholt\textsuperscript{147} once proposed the formation of periodic colloidal structures induced by long-range intermicellar interactions. However, in that case smaller aggregates at higher concentrations might be expected to show viscoelasticity as well, which is not always found. Hoffmann\textsuperscript{144,148} suggested that shear-induced phase transitions take place in dilute aqueous surfactant solutions. This suggestion is based on flow birefringence and rheological measurements. The anisotropic shape of the shear-induced structures is thought to be responsible for the viscoelasticity and birefringence.

3.2 Critical micelle concentrations and aggregation numbers of CTAB

Table 3.1 lists the cmc values of CTAB in the absence and presence of polymers. These cmc values were determined by conductivity measurements, which constitute a well-known method for study of ionic surfactants. Usually, a

<table>
<thead>
<tr>
<th>medium</th>
<th>cmc, mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>0.95\textsuperscript{b}</td>
</tr>
<tr>
<td>PVME</td>
<td>0.46</td>
</tr>
<tr>
<td>PPO</td>
<td>0.37</td>
</tr>
<tr>
<td>PEO</td>
<td>0.95\textsuperscript{b}</td>
</tr>
</tbody>
</table>

a) Polymer concentration: 0.5 g.dL\textsuperscript{-1}. b) Taken from ref. 68.
clear break is observed in the conductivity vs. concentration plot, indicative of the cmc. In the presence of PVME or PPO, however, the conductivity changes gradually. The most likely cause for this behavior is the fact that the degree of counterion binding is less for the polymer-bound than for the normal micelles. The reduction in counterion binding will be most pronounced just above the cmc when the polymer to micelle ratio is relatively large and the aggregation number relatively small compared to the ratio and aggregation number near saturation (vide infra). At increasing concentrations the aggregates grow and the counterion binding will increase in order to reduce electrostatic repulsion between the headgroups, which come nearer together. Furthermore, the cooperativity of the monomer-to-aggregate transition will be less for smaller aggregates and this will also widen the concentration range for the transition.

The hydrophobic polymers PVME and PPO induce a reduction in cmc, which points to polymer-micelle interaction. PEO does not exert any influence on the cmc. Though that observation does not exclude interaction (Chapter 2), literature data reveal that there is no interaction comparable to PEO/SDS or CTAB with hydrophobic polymers (section 3.1.2). However, some very weak interaction of PEO presumably with surfactant monomers may occur. PVP definitely does not associate with CTAB (section 3.1.2).

The aggregation numbers of CTAB micelles in the absence and presence of polymers have been measured as well, using the Turro and Yekta\textsuperscript{178} method, extended by Warr and Grieser\textsuperscript{120,151,179} for application to cationic and nonionic micelles. The method is based on static quenching of the fluorescent probe Ru(bipy)
\textsuperscript{2+} (1a) or an analog (1b) by the hydrophobic quencher

\[
\begin{align*}
1a & : R = H \\
1b & : R = n-C_{10}H_{21}
\end{align*}
\]
9-methylanthracene. It is required that both fluorophore and quencher are completely bound to the micelles according to a distribution following Poisson statistics. The static character of the quenching process implies that the distribution remains the same during the time needed for the excited probe molecule to relax to the ground state. Furthermore, a monodisperse size distribution of the micelles is tacitly assumed. In the case of anionic micelles, the probe 1a binds electrostatically. For nonionic and cationic micelles the amphiphilic analog 1b or a homolog is used, which binds hydrophobically.

If the fluorophore is only luminiscent when it occupies a micelle, devoid of quencher molecules, then the measured intensity ratio, $I([Q])/I(0)$, of the luminescence intensities in the presence of quencher to that in the absence of quencher, is determined by equation 3.1, in which $[Q]$ is the quencher concentration and $[M]$ the micelle concentration. The latter concentration is related to the surfactant concentration according to equation 3.2, in which $n$ is the aggregation number.

$$I([Q])/I(0) = \exp\left(-[Q]/[M]\right) \tag{3.1}$$

$$[M] = \frac{[\text{surfactant}]}{n} - \text{cmc} \tag{3.2}$$

The method is very practical. However its applicability is the subject of severe debate\textsuperscript{149-154}, and the method should be employed with care. Lianos and Zana\textsuperscript{149}, for instance, found a too low value for the aggregation number of SDS/NaCl using Ru(bipy)$_3^{2+}$/9-methylanthracene. This was attributed to a failure of the assumption of static quenching at high aggregation numbers\textsuperscript{150}. This failure and the errors induced by polydispersity do not immediately result in non-linear Stern-Volmer plots, which are used to obtain the aggregation number\textsuperscript{151} (Figure 3.3). Furthermore, high fluorophore-to-micelle ratios should be avoided\textsuperscript{152}, although later this prerequisite also has been disputed\textsuperscript{150}.

Another method that is often applied is based on pyrene excimer formation\textsuperscript{155-157}. Moroi et al.\textsuperscript{154} used both static quenching of Ru(bipy)$_3^{2+}$ and
pyrene excimer formation to obtain aggregation numbers for micelles of SDS and alkylsulfonic acids and found a satisfactory correspondence. Lissi and Abuin\(^6\) used the \(\text{Ru(bipy})_3^{2+}/9\)-methylandanthracene system for the determination of the aggregation numbers for PEO/SDS and PVP/SDS. If the experimental conditions are chosen with care, that is, low aggregation numbers and a low fluorophore concentration, good results can be obtained\(^{153}\).

A value of 70 (Table 3.2) was found for the aggregation number of CTAB micelles at 25 °C using quenching of the probe 1b. Other values reported in the literature\(^{33}\) include 54\(^{158}\) (steady-state fluorescence, pyrene); 88\(^{157}\), 90\(^{157}\), 82\(^{149}\) and 96 \(\pm 10\)\(^{159}\) (time-resolved fluorescence, pyrene); 104\(^{160}\)
Table 3.2  Aggregation numbers of CTAB in the absence and presence of polymers\textsuperscript{a} at various surfactant concentrations\textsuperscript{b}.

<table>
<thead>
<tr>
<th>[CTAB], mM</th>
<th>H\textsubscript{2}O</th>
<th>PVME</th>
<th>PPO</th>
<th>PEO</th>
<th>PVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>70</td>
<td>25</td>
<td>30</td>
<td>65</td>
<td>70</td>
</tr>
<tr>
<td>20</td>
<td>36</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>69</td>
<td>42</td>
<td>40</td>
<td>67</td>
<td>68</td>
</tr>
<tr>
<td>40</td>
<td>47</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>69</td>
<td>51</td>
<td>43</td>
<td>65</td>
<td>69</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Polymer concentration: 0.5 g.dL\textsuperscript{-1}. \textsuperscript{b}Temperature: 25 °C.

(time-resolved fluorescence, 1-methylpyrene/tetradecylpyridinium chloride); 80 ± 1\textsuperscript{161} (time-resolved fluorescence, 1,5-dimethylnaphthalene/cyclic azoalkane); 92\textsuperscript{157} and 95\textsuperscript{162} (light scattering); and 145\textsuperscript{127} (small angle neutron scattering). The reader will have noticed that a value must be grossly in error to fall outside the literature range (54-145). Several authors have questioned the use of pyrene for tetraalkylammonium surfactants since both specific interaction\textsuperscript{163} as well as the induction of micellar growth\textsuperscript{150,164} have been observed. Scattering techniques are only applicable to polymer-bound micelles if several conditions are met\textsuperscript{165}, which is probably not the case with hydrophobic polymers like PPO and PVME. The use of pyrene fluorescence in CTAB solution also has some disadvantages (vide supra). Therefore, we contend that quenching of 1\textsubscript{b} by 9-methylnaphthalene is a good choice and most likely suitable for studies of the influence of polymers on the aggregation number of CTAB micelles, as we have performed.

Addition of PVME or PPO results in a appreciable reduction of the aggregation number (n) (Table 3.2). Such a decrease in n has also been found for SDS in the presence of PEO\textsuperscript{57,64-66,165}, PVP\textsuperscript{64,66}, and PPO\textsuperscript{65,68}. We find that the aggregation number of CTAB micelles is not altered by the presence of PEO and PVP. This was anticipated since these polymers do not interact significantly with CTAB micelles. Reduction in n upon binding of the
hydrophobic polymers is understandable since the interacting polymers, which most likely reside at the hydrocarbon core-water interface\textsuperscript{54}, require space in order to keep headgroup-polymer repulsion to a minimum. The interheadgroup repulsion will be reduced, and the increased area of hydrophobic core-water contact will be shielded by the polymer. Altogether comparatively large surface-to-volume ratios of the micelles will be favored in the presence of an interacting polymer. This implies the formation of a smaller aggregate.

The dependence of \( n \) for the polymer-bound micelles on the surfactant concentration (observed for both CTAB/PVME and CTAB/PPO), has precedent in the literature on anionic micelles of SDS in the presence of polymers\textsuperscript{57,65}. Lissi and Abuin\textsuperscript{66}, however, have reported \( n \) values independent of the surfactant to polymer ratio (SDS/PEO and SDS/PVP) in the range of 40 to 100 % saturation of the polymer. The saturation concentrations for the combinations CTAB/PVME and CTAB/PPO are unknown. In comparison to SDS/PEO, and in view of the results presented in the next section, the polymer to surfactant ratios at which the aggregation numbers in Table 3.2 are measured, are likely to cover at least part of the range of 40 to 100 % saturation. The same applies for the aggregation numbers reported by Witte\textsuperscript{65,66} and others\textsuperscript{57,64}, so we conclude that the majority of the studies reveal a concentration-dependent \( n \) value. The polymer-bound aggregates probably grow as the degree of saturation of the polymer is increased due to a decrease of the local concentration of polymer segments at the micellar interface\textsuperscript{165}, and an increase in intermicellar repulsions. However, the listed aggregation numbers represent a number-average. Even if the size of the polymer-bound micelles were constant and free CTAB micelles of \( n = 70 \) were formed abruptly above the saturation concentration, a gradual increase in \( n \) with CTAB concentration would be observed \textit{above the saturation concentration}.

Altogether, it is clear that CTAB micelles interact with PVME and PPO, which results in a decrease in both the cmc and the \( n \) value, and the interaction process apparently closely resembles the interaction of polymers with micelles of SDS.
3.3 The sphere-to-rod transition of CTATs

One of the counterions that is able to induce the formation of rodlike micelles formed from cetyltrimethylammonium surfactants is tosylate. Sepulveda and coworkers\textsuperscript{166} first introduced CTATs for the measurement of the degree of dissociation of CTAX, in which X represents inorganic counterions. Later they studied the rheology of solutions of CTATs and of other CTAX surfactants. They also reported cmc values, degrees of dissociation, and the transfer free energy for the counterion from water to the micelle\textsuperscript{137}.

The tosylate ion is less rod-inducing than the salicylate (Sal) ion. As a result globular micelles of CTATs are initially formed above the cmc ($2.6 \times 10^{-4}$ M\textsuperscript{137a}). These micelles start to grow above a critical rod concentration (crc) of around 15 mM\textsuperscript{137}. Thus, CTATs provides the possibility of studying the sphere-to-rod transition and the influence of polymers on the concentration at which this transition takes place. In the case of CTASal rodlike micelles are formed directly above the cmc.

Sepulveda et al.\textsuperscript{137} established the transition concentration, by examining the increase in relative viscosity (crc ca. 20 mM), the decrease in partial molar volume (crc = 8-12 mM) and the break in the plot of UV absorbance versus concentration (crc = 15 mM). The observation that the transition concentration determined from viscosity data is higher than that determined by partial molar volume (or NMR line broadening) measurements is not a matter of serious concern. The cause for this common discrepancy is that the viscosity data reflect the interaction between rods and depend mainly on the overlap concentration whereas the other methods reflect changes in the local structure of the aggregate, such as surfactant packing and mobility.

We could not reproduce the break in UV absorbance around 15 mM, reported by Sepulveda\textsuperscript{137a}. The absorbance at 262 nm, the absorption maximum of a CTATs solution, measured using a cuvette with pathlength of 1 mm in order to keep the absorbance below 1 absorption unit, appeared to have a linear relation with the concentration of CTATs up to 30 mM. Since Sepulveda\textsuperscript{137a} did not state the wavelength at which his measurements were performed, a difference in wavelength between his and our measurements might lie at the origin of our
deviating results. However, we find it more likely that the break in absorbance found by Sepulveda\textsuperscript{137a} is due to a deviation from the Lambert-Beer law of the measured absorbances at high CTATs concentration and, concomitantly, high absorbances. Most spectrophotometers are linear up to 3 absorption units (A), for the very good ones this may be up to 5 A. The values reported by Sepulveda, however, go up to 9 A, with the break occurring at 4 A. This high value causes us to view his results with considerable reserve.

Another method that is often used to monitor the sphere-to-rod transition is line-broadening of the \textsuperscript{1}H-NMR signals\textsuperscript{142,145} of the alkyl chain protons of the surfactant upon rod formation. Figure 3.4 shows the concentration dependence of the combined line width of the resonances of the CH\textsubscript{2} and CH\textsubscript{3} groups of CTATs in D\textsubscript{2}O, at half height of the CH\textsubscript{3}-signal. Line-broadening

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.4.png}
\caption{The combined line width of the \textsuperscript{1}H NMR signals of the CH\textsubscript{2} and CH\textsubscript{3} groups, at half height of the CH\textsubscript{3} signal, of CTATs in D\textsubscript{2}O at 25 °C as a function of the CTATs concentration.}
\end{figure}
takes indeed place between 15 and 20 mM, which is in good accord with the results of the partial molar volume measurements of Sepulveda\textsuperscript{137a}. The NMR line-broadening method, however, was not reliable for measurements in the presence of PVME (or PPO), because of overlapping surfactant and polymer signals. Therefore, we used viscosity measurements to obtain the concentration at which the sphere-to-rod transition of CTATs takes place, in the absence and presence of PVME.

For these rheological measurements we used a shear-viscometer that can be equipped with different measuring devices. Two of these have been used, one having cone-and-plate geometry and the other cylindrical geometry. Provided that the rheometer is also equipped with a special sensor, the former allows the measurement of first normal stress differences\textsuperscript{167}, indicating viscoelasticity, as well as shear stress, from which the apparent viscosity can be calculated according to equation 3.3.

\[
\text{apparent viscosity} = \frac{\text{shear stress}}{\text{shear rate}}
\]  

(3.3)

The latter measuring device only allows the measurement of shear stress but produces more accurate data.

Usually the apparent viscosity of a solution of rodlike micelles drops rapidly when the shear rate is increased. (This, as well as other rheological peculiarities, will be discussed in more detail in section 3.4) Only at low shear rates (or at very high shear rates) is the viscosity Newtonian, that is, independent of shear rate. In Table 3.3 these low shear (Newtonian) viscosities are listed for solutions containing various concentrations of CTATs in H\textsubscript{2}O, and in the presence of 0.25 and 0.5 g.d\textsuperscript{-1} PVME (measured with cylindrical geometry). For the highly viscous solutions, shear rates as low as 6 x 10\textsuperscript{-3} s\textsuperscript{-1} have been used. It is hard to associate the sphere-to-rod transition to a well defined concentration, since the viscosity increases non-linearly with the CTATs concentration (Figure 3.5). The viscosity of a 15 mM CTATs solution in H\textsubscript{2}O is already four times as high as that of water (1 cP). At 18 mM CTATs, a first normal stress difference, indicating viscoelastic behavior and thus the presence of rods, can be observed above a
Table 3.3 Apparent viscosities of CTATs in aqueous solutions in the absence and presence of PVME at 25 °C.

<table>
<thead>
<tr>
<th>[CTATs], mM</th>
<th>( \eta_{\text{app}}, \text{Pa.s} )</th>
<th>( \text{H}_2\text{O} )</th>
<th>0.25 g.dl(^{-1}) PVME</th>
<th>0.5 g.dl(^{-1}) PVME</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0017</td>
<td>0.0016</td>
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<td></td>
</tr>
<tr>
<td>15</td>
<td>0.0046</td>
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</tr>
<tr>
<td>20</td>
<td>0.016</td>
<td>0.0047</td>
<td>0.0040</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.047</td>
<td>0.013</td>
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</tr>
<tr>
<td>30</td>
<td>0.53</td>
<td>0.081</td>
<td>0.021</td>
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<tr>
<td>35</td>
<td>5.09</td>
<td>0.24</td>
<td>0.067</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>1.28</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>3.55</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>10.01</td>
<td>2.54</td>
<td></td>
</tr>
</tbody>
</table>

Shear rate of 476 s\(^{-1}\) (using cone-and-plate geometry). Such viscoelastic behavior can also be observed visually as the recoil of trapped air bubbles when a swirling motion of the solution is abruptly stopped. From 20 mM CTATs onwards, thixotropic behavior is definitely displayed using a cone-and-plate measuring device (between 119 s\(^{-1}\) and 476 s\(^{-1}\)) and from 25 mM CTATs onwards using a cylindrical measuring device (between 60 s\(^{-1}\) and 119 s\(^{-1}\)). Thixotropic behavior is the occurrence of a decrease of the apparent viscosity with increasing time and is revealed in this case after a stepwise increase in shear rate (see, for example, Figure 3.10). The thixotropy as well as the viscoelasticity and non-Newtonian behavior are indicative for changes in the internal structure of the solution. Those changes originate from alignment and disruption of the rodlike micelles by the shear forces\(^{156,141,144,168-171}\).

Although the transition concentration for CTATs cannot be clearly defined it seems obvious from Figure 3.5 that the presence of PVME shifts the sphere-to-rod transition to higher concentrations. However, there may be a pitfall in this alluring conclusion. In 1985 Hoffmann et al.\(^{140}\) stated "that
Figure 3.5 The viscosity at low shear rates (Newtonian behavior) of CTATs in H₂O (○), 0.25 g.d⁻¹ PVME (■), and 0.5 g.d⁻¹ PVME (▲) at 25 °C, measured with cylindrical geometry. Extrapolation of the lines is based on the data from Table 3.3.

all theories which try to explain the viscoelastic properties of micellar solutions on models that are based on the existence of well-defined rods, without taking into account the transient nature of the micelles, sooner or later must fail". He illustrated this statement with the behavior of n-tetradecylpyridinium salicylate and n-tetradecylammonium salicylate. These compounds have similar cmc values, critical rod concentrations, and light scattering behavior, which suggests that the micellar structures and the interactions between them should also be the same. In spite of these similarities, the viscosities of aqueous solutions of these two compounds differ by almost two orders of magnitude. The differences between the
structural relaxation times of the micelles was shown to lie at the origin of this difference. For these surfactants the relaxation time stems from the kinetics of formation and dissociation of the micelle, whether stepwise per monomer or via coalescence or fragmentation of the entire micelle, and not from the rotation of the rods. Since this relaxation time may be influenced by the presence of additives\textsuperscript{131,148,172} such as \textit{n}-butanol or \textit{n}-pentanol, it is conceivable that the shift in concentration where the viscosity increase of the CTATs solution takes place, caused by PVME, is also due to these kinds of effects\textsuperscript{79,173} and not to a shift in concentration of the sphere-to-rod transition. However, we submit that this is not the case (vide infra) and that indeed a shift in transition concentration upon PVME transition takes place. We propose that PVME preferentially binds to spherical micelles of CTATs, for which the surface to volume ratio is more favorable for interaction with the polymer. Headgroup-headgroup repulsion and headgroup-adsorbed polymer repulsion will be less compared to those for polymer-bound rodlike aggregates, while the extra hydrocarbon core-water contact is stabilized by PVME. When the CTATs concentration exceeds the saturation concentration of PVME, free micelles will be formed, which grow into rods upon increasing the concentration.

This view is based on circumstantial evidence: (i) a reduction in the size of the aggregate is also found for CTAB micelles in the presence of PVME, (ii) the transition regions in the viscosity plots of the CTATs solution in H\textsubscript{2}O, 0.25 g.dL\textsuperscript{-1} aqueous PVME, and 0.5 g.dL\textsuperscript{-1} aqueous PVME are virtually superimposable, (iii) the shift in transition concentration is almost proportional with the polymer concentration, which points to saturation of the polymer playing a role, and (iv) in section 3.4 it will be shown that 0.5 g.dL\textsuperscript{-1} ethanol, \textit{t}-butanol or non-interacting polymers do hardly or not perturb the viscosity of a CTASal solution, contrary to interacting polymers such as PVME.

We draw the conclusion that rodlike micelles of CTATs are transformed (via the monomers) to polymer-bound spherical micelles in the presence of PVME. This is a novel finding in the field of polymer-micelle interactions.
3.4 The polymer-induced transition from a non-Newtonian to a Newtonian fluid

Cetyltrimethylammonium salicylate is the archetype of a cationic surfactant\textsuperscript{131} that forms rodlike micelles even in dilute (ca. 10\textsuperscript{-4} M) solutions\textsuperscript{119}. At higher concentrations CTASal solutions become viscoelastic and behave strongly non-Newtonian. The maximum in viscosity lies at a [Sal']/[CTA\textsuperscript{+}] ratio below one\textsuperscript{169,1}. One does not need special apparatus to observe the high viscosity and viscoelasticity of such a curious mixture. It is also easily seen that the presence of 0.5 g.dL\textsuperscript{-1} PVME or PPO completely eliminates the gel-like properties and reduces the viscosity to about that of water. Addition of the more hydrophilic polymers PEO or PVP does not induce such a transition. Although the change in the properties of the CTASal solutions induced by PVME or PPO strikes the eye, rheological measurements were performed to quantify the effect. As a matter of fact, the CTASal system spoils a beginning rheologist since the more attractive and special aspects of rheology are encountered without recourse to further examination of the field.

The same shear viscometer as used in the study of CTATs (section 3.3) was used. The (apparent) viscosities of micellar CTAB solutions in the absence and presence of sodium salicylate, polymers and low molecular weight additives are listed in Table 3.4. These values have been obtained using a measuring device with cylindrical geometry. The CTAB/NaSal solutions, whether or not in the presence of PVP, ethanol, or t-butanol, and, to a slightly lesser extent, CTAB/NaSal/PEO (20k), exhibit genuine non-Newtonian behavior. That is, the apparent viscosities\textsuperscript{167} vary dramatically with changing shear rate (Table 3.4, and Figures 3.6 and 3.7). The details of this behavior will be discussed

note (1): This observation seems to support Rao’s ‘string’-model\textsuperscript{135}, since intermicellar interactions induced by protruding salicylate ions are anticipated to be optimal below a complete saturation of the CTA\textsuperscript{+} micelle with salicylate ion. However, a second maximum in viscosity is observed in the presence of an excess of salicylate ions in the case of n-tetradecylpyridinium micelles\textsuperscript{169}.
Table 3.4 The effect of sodium salicylate and several monomeric and polymeric additives on the viscosity of a micellar CTAB solution.

<table>
<thead>
<tr>
<th>[CTAB], mM</th>
<th>[NaSal], mM</th>
<th>additive(a)</th>
<th>viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>15</td>
<td>PVME</td>
<td>1.08±0.02</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PEO</td>
<td>1.510±0.0006</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PVME</td>
<td>1.26±0.02</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PPO</td>
<td>2771(^b), 8.8(^c)</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PEO</td>
<td>1.630±0.006</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PPO</td>
<td>1.080±0.006</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PPO</td>
<td>274(^b), 16.9(^c)</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>PVP</td>
<td>2817(^b), 15.4(^c)</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>EtOH</td>
<td>3055(^b), 8.1(^c)</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>t-BuOH</td>
<td>2213(^b), 8.9(^c)</td>
</tr>
</tbody>
</table>

a) [additive\(]= 0.5 \text{ g.dL}^{-1}. \) b) Shear rate = 0.2985 s\(^{-1}\). c) Shear rate = 477.6 s\(^{-1}\).

later. By contrast, the apparent viscosities of CTAB/NaSal in the presence of PVME or PPO, and of CTAB solutions without NaSal, are orders of magnitude lower and are independent of shear rate, indicative of Newtonian behavior.

This polymer-induced transition from a non-Newtonian to a Newtonian fluid is, like in the case of CTATs, attributed to preferential binding of spherical rather than rodlike micelles onto the hydrophobic polymers. This is completely consistent with the reduction in aggregate size of CTAB micelles in the presence of PVME and PPO, and the shift to higher surfactant concentrations for the sphere-to-rod transition of CTATs by PVME. The hydrophilic polymers PEO and PVP do not bind CTAX micelles and, therefore, do not exert dramatic effects on the rheology of a solution of these aggregates.

Our results do not have any implication for the choice between 'strings-of-spheres' or 'rods' as model for CTASal aggregates. Interactions of strings-of-spheres with hydrophobic polymers would also be disastrous for
Figure 3.6 Double logarithmic plot of apparent viscosity vs. shear rate for the following aqueous solutions of CTAB (25 mM): no additives, (■); + PEO 20k (0.5 g.dL⁻¹), (▲); + PVME (0.5 g.dL⁻¹), (★); + NaSal (15 mM), (◇); + NaSal (15 mM) and PEO 20k (0.5 g.dL⁻¹), (△); and + NaSal (15 mM) and PVME (0.5 g.dL⁻¹), (○). The data were measured with cylindrical geometry.

their structural integrity. The aggregation number of the individual spheres would be expected to decrease, but, more importantly, the presence of polymer loops around the micelles would severely hamper string formation, and thus reduce the viscosity of the solution.

The shear rate dependence of the viscosity of the CTAB/NaCl solutions is not at all affected by PVP, ethanol, or t-butanol (Figure 3.6 and 3.7), and
Figure 3.7  Double logarithmic plot of apparent viscosity vs. shear rate for the following aqueous solutions of CTAB (25 mM)/NaSal (15 mM): no additives, (o); + PVP (0.5 g.dL$^{-1}$), (v); + ethanol (0.5 g.dL$^{-1}$), (A); + t-Butanol (0.5 g.dL$^{-1}$), (◊); + PPO (0.5 g.dL$^{-1}$), (•). The data were measured with cylindrical geometry.

only slightly by PEO. Generally speaking, three regions may be discerned in a plot of apparent viscosity versus shear rate$^{167}$. At very low shear rates, Newtonian behavior is displayed. Our data do not include low enough shear rates to observe this region. In the second region, the internal structure of the solution is altered by the shear forces. In the case of rodlike micelles, this causes a drop in apparent viscosity, due to aligning and disruption of the rods. This region is very obvious in Figures 3.6 and 3.7. In the third region, at high shear rates, the structural changes are completed and
Newtonian behavior can be observed again. For the present system, this transition occurs around a shear rate of 100 s\(^{-1}\). Wolff et al.\(^{174}\) reported the same shear rate of 100 s\(^{-1}\), above which Newtonian flow was observed for 20 to 25 mM CTAB containing 9 to 11.3 mM of 9-anthracenecarboxylic acid.

A closer inspection of our data in the second region, in which structural changes occur, leads to surprising results. In this region (below 84 s\(^{-1}\)), the shear stress (0.8 Pa, cylindrical geometry) does not change at all with changing shear rate (Figure 3.8), which implies a power law exponent of zero (see section 7.2). This is very un-liquid-like behavior. However, visual observation convinced us that the CTAB/NaCl solution is not a solid body. The shear stress obtained with cone-and-plate geometry reveals the same plateau

![Figure 3.8](image)

Figure 3.8 Double logarithmic plot of shear stress, measured with cylindrical geometry, vs. shear rate for aqueous solutions of CTAB (25 mM)/NaSal (15 mM) without additives (○) and in the presence of 0.5 g.dL\(^{-1}\) of PEO 20k (□).
region below 476 s\(^{-1}\) at a shear stress of 1 Pa (Figure 3.9). In the presence of PEO only a slight shoulder can be detected (Figure 3.8 and 3.9). This anomalous shear stress behavior has, to the best of our knowledge, only been noted before by Strivens\(^{141}\), also for the CTASal system. A phenomenon known as 'wall-slip'\(^{175}\) may lie at the origin of these observations. It is generally postulated that (apparent) slip effects are due to the formation of a thin low-viscosity fluid layer near the wall of the flow channel. We lack the necessary equipment to study this effect\(^{176}\). Wunderlich et al.\(^{170}\) tried to relate the dependence of the flow curve of a CTASal solution on the measuring

![Double logarithmic plot of shear stress vs. shear rate](image)

**Figure 3.9** Double logarithmic plot of shear stress, measured with cone-and-plate geometry, vs. shear rate for aqueous solutions of CTAB (25 mM)/ NaSal (15 mM) without additives (○) and in the presence of 0.5 g·dl\(^{-1}\) of PEO 20 k (●).
device to slip effects on the walls. The attempt was in vain, however, since the curves could not be explained in terms of the slip velocity concept.

A rate-independent shear stress is only expected for a solid body\textsuperscript{167}, which clearly does not apply for a CTAB/NaCl solution, as mentioned before. A definite feature of the liquid-like properties of this solution is the observation of thixotropy (Figure 3.10) and rheopexy. Rheopexy (the opposite of thixotropy) denotes an increase in viscosity with increasing time at a constant shear rate. For CTAB/NaCl solutions, this is observed upon stepwise decreasing the shear rate. It results from the reversibility of the alignment and breakdown of the rodlike micelles. For the CTAB/NaCl solution thixotropy

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{thixotropic_behavior.png}
\caption{Thixotropic behavior of CTAB (25 mM)/ NaSal (15 mM)/ PEO 20k (0.5 g.dl\textsuperscript{-1}). At $t = 0$ min., the shear rate is switched from 1.19 to 2.38 s\textsuperscript{-1}.}
\end{figure}
and rheopexy is observed below a shear rate of 476 s\(^{-1}\), and for the CTAB/NaSal/PEO system below 76 s\(^{-1}\) using cone-and-plate geometry. The disappearance of these phenomena coincides with the end of the shear stress plateau. The 3 to 5 minutes, which are needed in the case of stepwise increased shear rates, are normal times for CTASal solutions\(^{141}\) and are not greatly affected by PEO.

The visually observed viscoelasticity has also been quantified through the measurement of first normal stress differences using cone-and-plate geometry (Figure 3.11). Especially at shear rates below 2000 s\(^{-1}\), the first

![Figure 3.11](image)

**Figure 3.11** Plot of first normal stress difference, indicating viscoelasticity, vs. shear rate, for aqueous solutions of CTAB (25 mM)/ NaSal (15 mM) without additives (○) and in the presence of 0.5 g.dl\(^{-1}\) PEO 20 k (△). The uncertainty of the data is ca. 50 Pa.
normal stress differences of the CTAB/NaSal solution, in the presence of PEO, are significantly larger than those of the aqueous CTAB/NaSal solution. However, below 200 s\(^{-1}\) in the presence of PEO, the first normal stress difference drops sharply to values that are too low to measure. The higher first normal stress difference of the CTAB/NaSal/PEO solution compared to that of the CTAB/NaSal solution is probably related to the fact that the viscosity of the former solution is also higher in this range of shear rate (Figure 3.6).

The (slight) influence of PEO on the rheology of the CTAB/NaSal solution may be due to (i) interference of the polymer chains with the intermicellar ordering and flow of the rods, or (ii) to a modest interaction of PEO with CTAX monomers or aggregates either influencing the structural relaxation time or the structures themselves. There appears to be no reason, however, why interference should occur for PEO but not for PVP, whereas there are indications that PEO has a very small but detectable effect on CTAB aggregation, which PVP has not (see section 3.1.2). Thus the latter explanation is more likely.

We conclude that PVME and PPO induce a breakdown of rodlike micelles of CTASal into polymer-bound spherical micelles, while PVP, ethanol, and \(t\)-butanol do not affect the rods at all. Presumably, PEO undergoes a modest interaction with CTASal, which results in a slight altering of the detailed rheology.

3.5 Experimental section

Materials. CTAB (Merck) was purified as described by Duynstee and Grunwald\(^{177}\). CTATs (Sigma), NaSal (Merck), and PPO (weight-averaged mw 1,000, Aldrich) were used as received. PEO (Fluka) and PVP (Kolloidon-90, BASF) were purified as described in Chapter 2. PVME (50 % (w/w) solution in water, inherent viscosity 0.57, Aldrich) was freeze-dried. The yellowish residue was dissolved in ethanol and heated with activated carbon. After filtration, the solvent was evaporated and the residue was dissolved in water, dialyzed and freeze-dried.
The polymer was stored as a 20 % (w/w) solution in water. The molecular weight of PVME (27,000) was determined by viscosity measurements in butanone. The intrinsic viscosity equals $K \times (\text{mw})^{\alpha}$, in which $K = 137 \times 10^{-3}$ mL.g$^{-1}$ and $\alpha = 0.56$ at $30^\circ C$ for this combination of polymer and solvent.

The quencher 9-methylanthracene (Janssen) was used as received. The fluorophore bis(2,2'-bipyridyl)-mono(4,4'-didecyl-2,2'-bipyridyl)ruthenium(II) perchlorate was a gift from Dr. L.A.M. Rupert of the Koninklijke/ Shell Laboratorium, Amsterdam. The water used in all experiments was demineralized and distilled twice in an all-quartz distillation unit.

**Conductivity measurement.** Conductivities were measured using a Wayne-Kerr Autobalance Universal Bridge B642 fitted with a Philips electrode PW 9512101 with a cell constant of 0.71 cm$^{-1}$. The solutions were thermostated in a cell at $25 \pm 0.1 ^\circ C$ for at least 15 min. before measurements were initiated. The conductivity cell was equipped with a magnetic stirring device. The surfactant concentrations were varied by the addition (micro-syringe) of appropriate portions (10 to 50 µl) of a concentrated solution of the surfactant to the conductivity medium. Concentrations were corrected for volume changes. Cmc values were taken from the intersection of the tangents drawn before and after the first break in the conductivity vs. concentration plot. In the case of PPO and PVME solutions no clear break could be observed since the conductivity varies non-linearly with the concentrations above the cmc. In these cases, the cmc values were taken from the discontinuity in the plot of the first derivative of the conductivity vs. the concentration. These values deviate from those determined by Witte$^{68}$, who took the observed deviation from the first linear part of the conductivity plot.

**Fluorescence measurements.** Stock solutions of fluorophore and quencher were prepared in 96 % Uvasol-grade ethanol (Merck). In a typical experiment, 2 µl of the fluorophore stock solution was injected into 2 ml of the surfactant solution, yielding a probe concentration of $10^{-5}$ to $10^{-6}$ M. Subsequently 2 µl aliquots of the appropriate quencher solution were injected. The concentration of the quencher solution was chosen to yield a quencher-to-micelle ratio of

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ca. 0.8 after injection of between 8 and 20 µl. The solution in the cuvette was stirred with a magnetic device, and thermostated at 25 ± 0.1 °C. Fluorescence intensities were measured using a SLM-Aminco (SPF-500C) spectrofluorometer. Excitation and emission wavelengths were 453.5 nm and 626 nm, respectively. The aggregation numbers were determined from plots of ln I(0) - ln I([Q]) versus [Q] / ([CTAB] - cmc) according to the method of Turro and Yekta.\textsuperscript{178}

**UV measurements.** UV measurements were performed on a Perkin-Elmer λ5 spectrophotometer, using cuvettes with a 1 mm pathlength. Some practice in inserting cuvettes in the cuvette-holder of the spectrophotometer is needed to obtain results that are reproducible to within 0.001 A.

**Rheological measurements.** Solutions were prepared at least one hour in advance. CTATs solutions were prepared by dilution of a clear stock solution of 40 mM CTATs with either water or an aqueous polymer solution. CTASal solutions were prepared from appropriate fresh stock solutions of CTAB, NaSal, and polymer. Rheological measurements were performed on a Brabender Rheotron rheometer with either cone-and-plate geometry (P7) or cylindrical geometry (A1). The rheometer was equipped with a Normal F-sensor which allows the measurement of first normal stress differences when cone-and-plate geometry is used. The sample solution was thermostated at 25 ± 0.1 °C during the measurements.