Rheology, Cryogenic Transmission Electron Spectroscopy, and Small-Angle Neutron Scattering of Highly Viscoelastic Wormlike Micellar Solutions

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To understand the strong viscoelastic response showed by aqueous solutions of erucylbis(hydroxyethyl)-methylammonium chloride (EHAC) in the presence of potassium chloride (KCl), steady-state rheology, small-angle neutron scattering (SANS), and cryogenic transmission electron microscopy (cryo-TEM) experiments were performed. This cationic surfactant has the ability to self-assemble into giant wormlike micelles. The effect of surfactant concentration, added salt, and temperature were investigated. The surfactant solutions have a gellike behavior at room temperature and become Maxwellian as the temperature is increased. It was found that the low-shear viscosity has a strong dependence on salt concentration and temperature. Small-angle scattering indicated the formation of wormlike micelles. The high-Q range was fitted using the Kratky−Porod wormlike chain model, and a cross-sectional radius of gyration ($R_{g,xs}$) of 21 Å was obtained. Additionally, cryo-TEM images revealed changes in the structure of the entangled network with the addition of salt.

Introduction

Surfactants in solution are known to adopt an impressive polymorphism of structures or aggregates.[1] Cationic surfactants can self-assemble into long, flexible wormlike micelles under certain conditions of salinity, temperature, presence of counterions, etc., and the entanglement of these micelles into a transient network imparts useful viscoelastic properties to the surfactant solutions which are analogous to those observed in solutions of flexible polymers. However, unlike ordinary polymers, wormlike micelles are in equilibrium with their monomers and micellar chains can reversibly break and recombine on a time scale that is dependent on the system and the prevailing physicochemical conditions.[2−4]

It is well-known that the low shear rate viscosity (η_o) of many surfactant solutions strongly depends on salt concentration. Usually, the viscosity first increases with increasing salt concentration, going through a maximum, and then decreases.[2,3,5,6] Aqueous solutions of ionic surfactants can undergo uniaxial growth upon the addition of salt. As a result, an increase of micellar length is promoted, the viscosity of the solution increases, and the micelles form an entangled network.[3,5−7] The decrease in viscosity with further addition of salt, however, is more difficult to explain. Several authors[1,3,8,9] have proposed

that this decrease at high salt concentrations may be due to the formation of a multiconnected network in which stress relaxation can occur by the sliding of cross-links along the wormlike micelles. Thus, the maximum in viscosity with increasing salt concentration may indicate a shift from linear to branched micelles. Branching is expected to occur when the free energy cost associated with the cross-link formation becomes comparable to that needed for the formation of end caps.

A multiconnected branched micellar network and an entangled micellar network cannot be distinguished from one another directly by scattering techniques, such as neutron and light scattering.[8] A microstructural model must be assumed and its validity tested by comparison of the predicted and measured scattering patterns. It is, therefore, desirable to visualize the microstructure directly and to use this information as a guide to quantitative analysis with the scattering data. This is particularly useful when one can distinguish elongated micelles that may be more wormlike than rodlike.[9]

Cryogenic transmission electron microscopy (cryo-TEM) is a technique suitable for direct visualization of surfactant aggregates formed in solutions and is the only available technique to unambiguously distinguish between branched and unbranched micelles.[8,11−15] Cryo-TEM has been used successfully to explore the spherical to wormlike transition of surfactant solutions, as in the work of Lin et al.[8,12,13]

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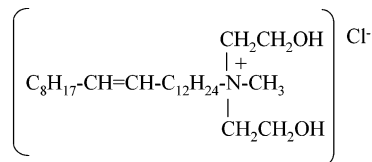
With this method thin films of a liquid sample are prepared in a controlled environment chamber, in which the sample is rapidly frozen and the water is vitrified so that the structural details of the micelles embedded in it will not be obscured, and one can observe the microstructure in an electron microscope with a cold stage that keeps the sample near the temperature of liquid nitrogen. By this method, one can accurately control the temperature and the humidity of the system prior to rapid freezing.[10]

Raghavan et al.[2] studied the rheological response of a cationic surfactant with a long unsaturated tail [erucylbis-(hydroxyethyl)methylammonium chloride (EHAC)] in the presence of sodium salicylate (NaSal) or sodium chloride (NaCl) at 25 °C. The surfactant solutions exhibit very high relative viscosities ($\approx 10^7$) or gellike behavior at room temperature, and they retain appreciable relative viscosities ($> 10^4$) for temperatures up to ca. 90 °C. However, much higher concentrations of NaCl are required to produce high viscosities compared to those obtained by addition of NaSal. This is because while salicylate counterions can penetrate between the headgroups into the hydrophobic core of the micelles, the Cl^- counterions cannot do so. Additionally, it was found that the molecular structure of the surfactant leads to a high-energy cost for micellar scission (160 kJ/mol). As a consequence, the thermodynamic balance favors micellar growth, resulting in extremely long wormlike micelles. Thus, an entangled network of such micelles can account for the strong viscoelasticity of the system. Additionally, EHAC solutions show a viscosity maximum as a function of salt concentration, which may in part be due to a transition from linear to branched micelles or a maximum in micellar contour length.

The aim of this work is to understand the strong rheological response of aqueous solutions of EHAC in the presence of KCl. The effects of added salt, temperature and surfactant concentration were investigated using steady-state rheology, small-angle neutron scattering (SANS), and cryogenic transmission electron microscopy (cryo-TEM). The combination of these techniques provided a good understating of the rheological response of the system.

Experimental Section

Materials. The chemical structure of the viscoelastic surfactant erucylbis(hydroxyethyl)methylammonium chloride (EHAC) is shown below.[2] It was obtained from Schlumberger

$$\left[\begin{array}{c} CH_2CH_2OH \\ | + \\ C_8H_{17}\text{-}CH=CH\text{-}C_{12}H_{24}\text{-}N\text{-}CH_3 \\ | \\ CH_2CH_2OH \end{array} \right] \; Cl^-$$

Cambridge Research Limited. The bulk density of the surfactant is 950 kg·m^{-3} (quoted by manufacturer). Potassium chloride (KCl) was purchased from Aldrich with a purity of 99+ wt %. Samples were prepared by weighting the appropriated amounts of surfactant, salt, and deionized water. After mixing, the samples were heated at 60 °C for 15 min to remove any entrained air bubbles.

The solutions made for the SANS experiments were prepared in deuterium oxide (D_2O) instead of deionized water (GOSS Scientific Instruments Ltd., 99.9 at. wt % D).

Rheology. Rheological measurements were carried out on a controlled stress Bohlin Instrument (CVO). The shear stress was varied between 0.06 and 80 Pa to obtain shear rates between 0.0003 and 600 s^{-1}. The shear stress dependence was monitored as a function of increasing and decreasing shear stress (up/down ramp). No effects of hysteresis were seen. A Couette geometry (C25) with cup 27.5 mm diameter, bob 25 mm diameter, and height 37.5 mm was used for the high viscosity samples. For the low viscosity samples, the double gap geometry (DG40/50) was used with an external gap 4.54 mm, an internal gap 3.98 mm, and height 46 mm. Steady-state measurements were performed at different temperatures ranging from 40 to 80 °C given an equilibration time of 200 s at each shear stress. A solvent trap was used to minimize changes in composition due to water evaporation. The surfactant concentration was varied between 0.25 and 4.5 wt % and the salt concentration varied from 2 to 12 wt %.

The zero-shear viscosity (η_o) was obtained by fitting the steady-state-rheology data into the Carreau model,[16] given by the following equation:

$$\eta(\gamma) = \frac{\eta_o}{\left[1 + \left(\dfrac{\dot{\gamma}}{\dot{\gamma}_c} \right)^2 \right]^{n/2}} \tag{1}$$

where n is an exponent describing the shear-thinning behavior and ($\dot{\gamma}_c$) is the critical shear rate.

Small-Angle Neutron Scattering (SANS). Neutron scattering experiments were performed at the ISIS facility, Rutherford Appleton Laboratory, UK, and Forschungszentrum Jülich, Germany. The LOQ instrument at ISIS uses incident wavelengths between 2.2 and 10 Å sorted by time of flight with a sample detector distance of 4.1 m. This gives a Q range between 0.006 and 0.24 Å^{-1}. On the KWS-2 instrument at Jülich, the Q range is given by the sample detector distance using a fixed wavelength. In this experiment, the sample detector distances used were 2 and 8 m with a wavelength of 7 Å. This gives a Q range between 0.006 and 0.140 A^{-1}. The solutions were placed in quartz cells with a 2 mm path length. The surfactant concentration was varied from 0.25 to 4.5 wt % and the salt concentration was varied from 0.1 to 12 wt %. The scattering length densities of the surfactant and D_2O are 6.07×10^{-9} and 6.37×10^{-6} Å^{-2}, respectively. The raw scattering spectra were corrected for background radiation, detector efficiency, empty cell scattering, transmission, and electronic noise by conventional procedures. The experiment was done at 25 and 40 °C.

In the high-Q range the scattering data can be analyzed to obtain information on the local structure. Parameters such as the cross-sectional radius of gyration ($R_{g,xs}$) and the mass per unit of length (M_L) can be found by employing the Kratky–Porod wormlike chain model approximation[17,18] given by

$$I(Q) = \frac{\pi c (\Delta \rho_N)^2 M_L}{N_A \rho_B^2 Q} \exp\left[-\left(\frac{Q^2 R_{g,xs}^2}{2} \right) \right] \tag{2}$$

where ρ_B is the bulk polymer density (kg·m^{-3}), N_A is Avogadro's number, $\Delta \rho_N$ is the scattering length density (Å^{-2}), and c is the surfactant concentration (kg·m^{-3}).

Cryo-TEM. Cryogenic transmission electron microscopy (cryo-TEM) investigations were performed with a Zeiss EM 902A instrument, operating at 80 kV and in the filtered bright-field mode at $\Delta E = 0$ eV (electron energy loss normal to the bright-field imaging). Digital images were recorded under low dose conditions with a BioVision Pro-SM Slow Scan CCD camera system. To enhance the image contrast, an underfocus of 1–2 μm was used. The preparation procedure has been described in detail in a recent review.[19] Specimens for examination were

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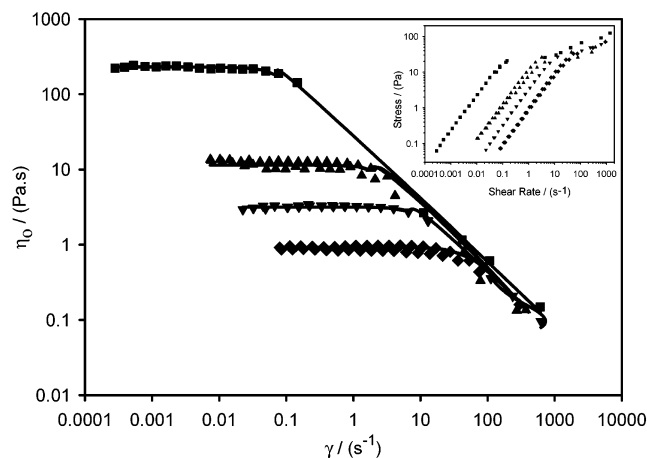
Figure 1. Rheograms for the system containing 4.5 wt % EHAC and 6 wt % KCl at different temperatures. Insert: Shear-banding phenomena in this system. (■, 40 °C; ▲, 60 °C; ▼, 70 °C; ◆, 80 °C; and —, Carreau model.)

Figure 2. Dependence of low-shear viscosity (η_o) on salt concentration (KCl) using different surfactant concentrations at a fixed temperature of 40 °C. ●, 4.5 wt %; ■, 3.5 wt %; ▲, 2.5 wt %; ▼, 1.5 wt %; ◆, 0.5 wt %; +, 0.25 wt %.

prepared in a climate chamber in which the temperature and humidity can be controlled. The temperature in the chamber was set to 25 °C and the relative humidity to approximately 99%. Thin films of sample solution were formed by placing a small drop of the liquid on a perforated polymer support film, which had been mounted on a standard copper grid and thereafter coated with carbon on both sides. After the drop was blotted with filter paper, thin sample films (10−500 nm) spanned the holes in the support film. Immediately after blotting, the sample was vitrified by plunging it into liquid ethane. Samples were kept below −165 °C and protected against atmospheric conditions during both transfer and examination.

Results and Discussion

Rheological Measurements. It is well-known that some cationic surfactants can self-assemble into long, flexible wormlike micelles in the presence of salt, and the entanglement of these micelles into a transient network gives viscoelasticity to the surfactant solutions. At room temperature the surfactant solutions are gellike with high low-shear viscosities and the Newtonian plateau is shifted to very low shear rates, making it difficult to detect experimentally. This is likely to be one indication that this system could form very long wormlike micelles (see Cryogenic Transmission Electron Microscopy section below). The entangled network of such micelles may have long relaxation times, which may fall outside the accessible measurement scales. However, as the temperature is increased, the rheology becomes characteristic of a Maxwellian fluid with a critical shear rate and relaxation time.[2,3] In this study we focus on this region (above 40 °C). The viscosity as a function of shear rate and temperature is presented in Figure 1 for the system containing 4.5 wt % EHAC and 6 wt % KCl. The fluid rheogram is characterized by a high viscosity region at low shear rates, in which the surfactant solutions display a Newtonian behavior and a shear-thinning region where a drop in viscosity is observed. The high viscosity observed in the Newtonian plateau can be interpreted as the result of the presence of an entangled network of wormlike micelles. The shear-thinning region is more complicated to explain. It is believed that the entangled network of wormlike micelles is aligned as the shear rate increases[2,20] and the surfactant solution starts to shear-thin. However, above a critical shear rate the solutions cannot reach steady state and a dramatic drop in viscosity is observed leading
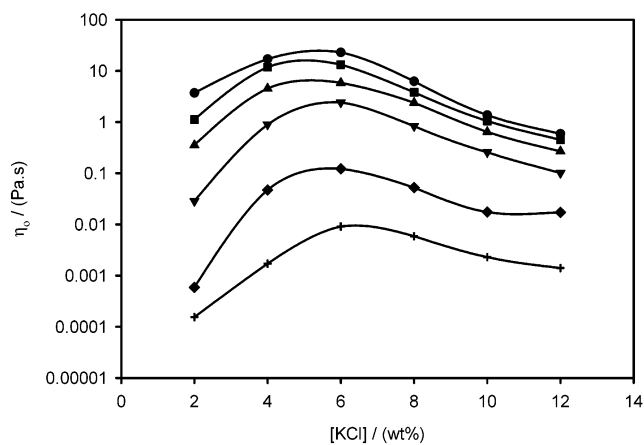
to a stress plateau (insert Figure 1). The usual explanation for this stress plateau is shear banding as described by several authors in the literature.[20−24] Such bands are believed to be associated with the coexistence of regions of different shear rates within the sample (visual observation during the rheological measurements). The presence of shear banding will depend on surfactant concentration, salt concentration, and temperature. From the insert in Figure 1 it can be seen that as the temperature is increased this effect is no longer present in the system. More studies are required to understand this type of flow instability in EHAC surfactant solutions.

The Carreau model[16] was used to obtain the zero-shear viscosity (viscosity at the plateau, η_o) and not to describe the shear-thinning behavior, and it can be seen (Figure 1) that there is a good correlation between the experimental data and the model.

For many surfactant systems,[2,3,5,6,25−28] it has been observed that the low-shear viscosity increases with salt concentration, reaching a broad maximum and then decreasing at high ionic strength. This behavior is also observed in solutions of EHAC at various concentrations, as shown in Figure 2. The increase in the low-shear viscosity with increasing salt concentration has been explained in terms of micellar growth. Increasing the amount of salt leads to an increase in the curvature energy of the surfactant molecules in the end caps, relative to that of the molecules in the cylindrical body of the micelles. As a consequence, an increase in micellar length is promoted, the viscosity is raised, and the micelles start to overlap, forming an entangled network. Several authors[1,9,25,29] have suggested that the decrease in viscosity at high salt content may be due to the formation of branched wormlike micelles. The cross-links in the resulting multiconnected micellar network can slide along the micelles and hence serve as stress release points. Such

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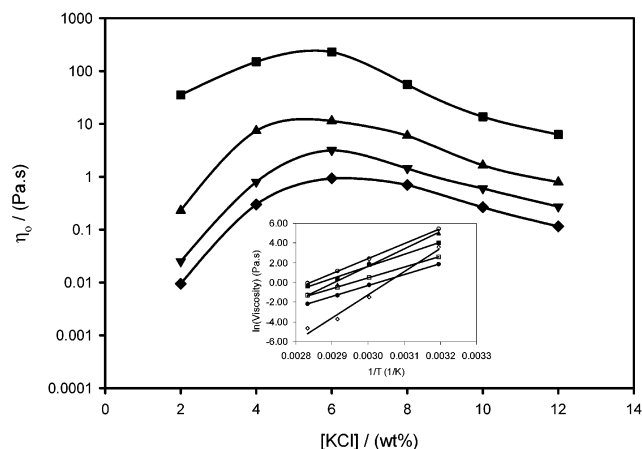
Figure 3. Low-shear viscosity (η_o) as a function of salt content and temperature at a fixed surfactant concentration of 4.5 wt % (■, 40 °C; ▲, 60 °C; ▼, 70 °C; ◆, 80 °C). Arrhenius behavior (insert) for low-shear viscosity (◇, 2 wt % KCl; ▲, 4 wt % KCl; ○, 6 wt % KCl; ■, 8 wt % KCl; □, 10 wt % KCl; ◆, 12 wt % KCl).

a branched micellar network will therefore show a reduced viscosity compared to that of the entangled linear micelles. Thus, the maximum in viscosity with increasing salt concentration is expected to correspond to a shift from linear to branched micelles.

Additionally, it can be seen from Figure 2 that the low-shear viscosity decreases by lowering the surfactant concentration in the samples. At low surfactant concentrations, short rodlike micelles are formed which have a weak rheological response (low viscosity) compared to those formed at higher surfactant concentration. For the latter, 6−8 wt % salt is required to reach the maximum in viscosity and a shift in the low-shear viscosity is observed at 40 °C for 0.25 wt % surfactant concentrations. Therefore, while 2 wt % KCl concentration is sufficient to promote a significant increase in the viscosity (growth of the micelles) for surfactant concentrations between 0.5 and 4.5 wt %, the same salt concentration does not have a similar effect at low surfactant concentrations. In that case, short wormlike micelles are formed and a weak rheological response is observed.[1,29] Higher viscosities can be obtained for this system using a binding salt such as sodium salicylate (NaSal), as reported by Raghavan et al.[2]

In Figure 3, the low-shear viscosity as a function of salt content and temperature is presented at a fixed surfactant concentration of 4.5 wt %. As the temperature is increased, the viscosity is seen to decrease. From the literature[1−3,25,30] it is known that the micellar contour length ($\bar{L}$) decreases with increasing temperature according to the following equation:

$$\bar{L} \approx \phi^{1/2} \exp\left(\frac{E_a}{k_B T}\right) \tag{3}$$

Here E_a is the activation energy and ϕ is the surfactant concentration. The dependence of the low-shear viscosity on temperature is a consequence of the decrease in the micellar contour length of the micelles. Semilogarithmic plots of η_o versus $1/T$ (insert, Figure 3) fall on a straight line, thus revealing an Arrhenius behavior. The values of the activation energy were estimated from the slope of these plots.

The dependence of the activation energy on salt and surfactant concentrations is presented in Table 1. The

Table 1. Activation Energy (kJ/mol) for 4.5 wt % EHAC Micelles between 40 and 80 °C as a Function of Salt and Surfactant Concentration

KCl (wt %)	E_a (kJ/mol)
2	195.13
4	146.89
6	126.70
8	102.85
10	91.22
12	92.46

values of E_a are in agreement with the values reported for other micellar systems.[2,25,30,31] An interesting observation is that the activation energy decreases as a function of KCl concentration. According to Fischer et al.,[31] the activation energy describes the energy that it is necessary to move individual micelles in an environment of surrounding micelles. The activation energy is therefore given by the interactions between individual aggregates. Following this idea, it seems that there is a first region (≈ 2 wt % KCl) where the charge properties of the micellar surface are such that the wormlike micelles resist interaction and fusion with the surrounding micelles. Additionally, their movements are constrained by entanglements with other wormlike micelles, giving rise to a high E_a. In contrast, at intermediate salt concentration (4 wt % KCl), the wormlike micelles have a lower surface charge such that the worms can fuse, break, and re-form more easily. Therefore, the activation energy decreases. At high salt concentration (≥ 6 wt %), a micellar branched network is formed. As a consequence, the cross-links in the network can slide along the micellar chains giving them enhanced mobility and resulting in a further decrease in E_a and viscosity. Another possible explanation of this trend could be related to a maximum in the contour length of the micelles. According to eq 3 the logarithm of the length of the micelles is proportional to the activation energy. Therefore, at 2 wt % KCl, the highest value in activation energy might correspond to a maximum in contour length of the wormlike micelles. Thus, the energy to form new end caps is extremely high and the micelles start to form branching points.

Small-Angle Neutron Scattering. Figure 4 shows the scattering intensity curves obtained for EHAC micelles in D_2O with a surfactant concentration varying between 0.25 and 4.50 wt % at 25 °C. A sharp scattering peak is observed that moves to higher Q values as the surfactant concentration increases. The distance between the micelles formed in solution is decreasing (shift in the peak) and the interactions between the micelles become stronger as the concentration of surfactant is increased. A polydisperse core−shell model combined with the Hayter Penfold micellar interaction model[32] was used to fit the experimental data. The model appears to be in good agreement with the data, revealing that a spherical micellar structure is formed for all surfactant concentrations, with an inner radius of 29.8 ± 0.5 Å and an outer radius of 34.7 ± 0.3 Å.

Figure 5 shows the scattering curves for 4.5 wt % EHAC solutions upon the addition of small quantities of KCl at 40 °C. It is clear that the structure peak gradually disappears with increasing the amount of salt in the system until the shape of the scattering curve decays, approaching a Q^{-1} behavior (rods). The presence of the electrolyte screens the interactions between micelles and promotes micellar growth.[3] Therefore, the scattering peak

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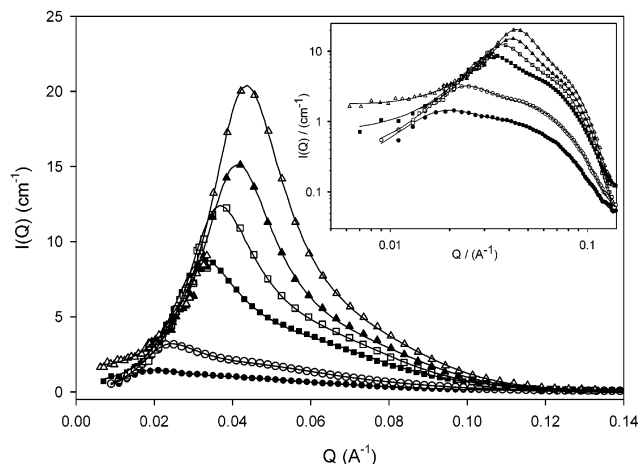(32) Cosgrove, T. Insanity program.

Figure 4. Scattering curves obtained for EHAC micelles in D_2O without added salt at 25 °C. The error bars are comparable in size with the experimental points. Insert: Logarithmic scale. ($\triangle$, 4.5 wt %; $\blacktriangle$, 3.5 wt %; $\square$, 2.5 wt %; $\blacksquare$, 1.5 wt %; $\bigcirc$, 0.5 wt %; $\bullet$, 0.25 wt %; —, core–shell model.)
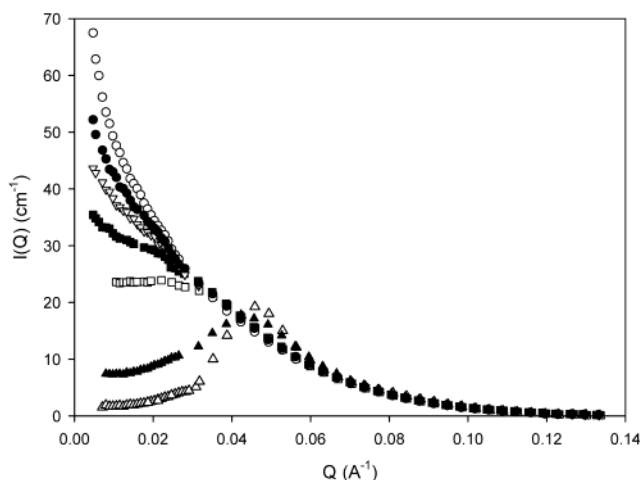

Figure 6. Scattering intensity $I(Q)$ versus scattering vector Q for polymer-like micelles formed by 4.5 wt % EHAC in D_2O as a function of KCl content at 40 °C. ($\bigcirc$, 2 wt % KCl; $\bullet$, 4 wt % KCl; $\square$ 6, wt % KCl; $\blacksquare$, 8 wt % KCl; $\triangle$, 10 wt % KCl; $\blacktriangle$, 12 wt % KCl; —, Kratky–Porod model.)

Figure 5. Scattering intensity $I(Q)$ versus scattering vector Q for polymer-like micelles formed by EHAC in D_2O as a function of KCl content at 40 °C. ($\triangle$, no KCl; $\blacktriangle$, 0.10 wt % KCl; $\square$, 0.25 wt % KCl; $\blacksquare$, 0.50 wt % KCl; $\triangledown$, 0.75 wt % KCl; $\bullet$, 1.0 wt % KCl; $\bigcirc$, 2 wt % KCl.)

Figure 7. Cryo-TEM micrographs of wormlike micelles formed by EHAC with (A) no KCl, (B) 2 wt % KCl, (C) 6 wt % KCl, and (D) 12 wt % KCl. Scale bar = 100 nm.

is no longer present at 2 wt % KCl and a change from spherical micelles to wormlike micelles takes place.

At intermediate and high salt concentrations, it can be seen from Figure 6 (40 °C) that at low-Q values (insert) the scattering intensity continues to increase with salt concentration. This is an indication of the continued growth of the wormlike micelles upon the addition of salt, resulting in an increase in their contour length. In contrast, in the high-Q range all the scattering curves superimpose, suggesting that the local micellar structure does not change upon further addition of salt. This is due to the fact that micellar growth occurs in a one-dimensional fashion along the micellar contour and leaves the cylindrical cross section unaltered.[29,33–35]

As the local micellar structure remains constant upon the addition of salt (high Q), the experimental data can be analyzed to obtain the cross-sectional radius of gyration, $R_{g,xs}$, of the wormlike micelles and the mass per unit of
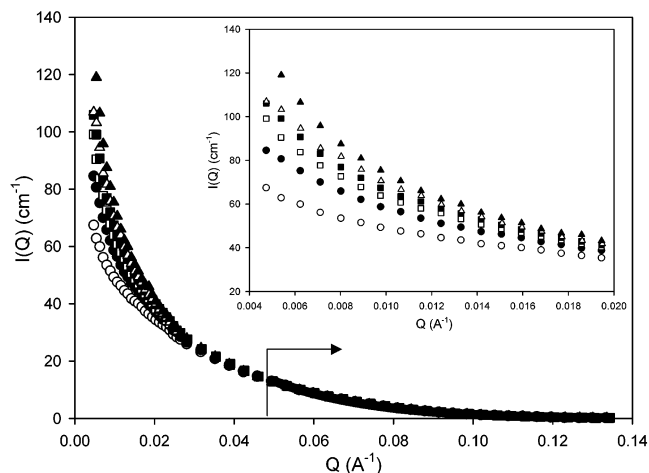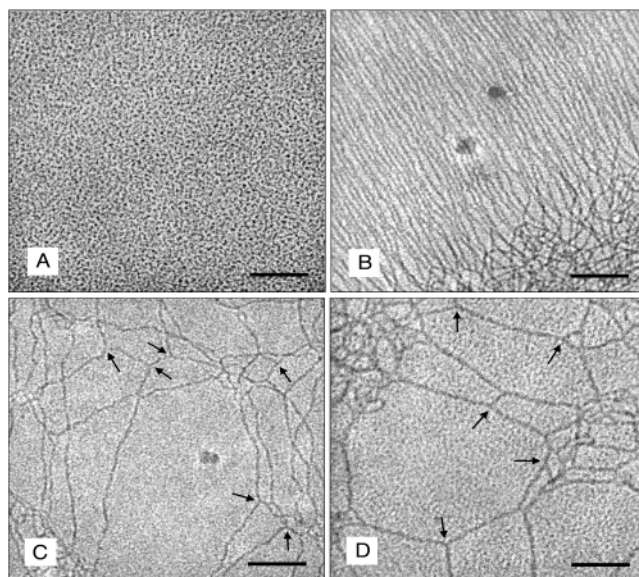
length, M_L, by employing the Kratky and Porod wormlike model given by eq 2.[32] The values obtained for $R_{g,xs}$ and M_L are 21 ± 0.1 Å and (1.90 ± 0.03) × 10^{-13} g/cm, respectively, and they are in the range of values reported in the literature for wormlike micelles formed by ionic surfactants.[33,36,37]

Cryogenic Transmission Electron Microscopy. Direct images of vitrified samples of EHAC/KCl were obtained by cryo-TEM. Figure 7 presents a set of cryo-TEM micrographs of the vitrified 4.5 wt % EHAC solutions containing no KCl, 2 wt % KCl, 6 wt % KCl, and 12 wt % KCl, respectively. Figure 7A shows the spherical micelles predicted by small-angle neutron scattering.

When salt is added to the system (Figure 7B, 2 wt % KCl), very long wormlike micelles are formed. The wormlike micelles overlap and become entangled (bottom right corner). As a consequence, it is impossible to identify

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where they begin and end. The wormlike micelles shown in this micrograph (Figure 7B) are not branched; one indication of this is shown in the image. As it is possible to align the wormlike micelles without breaking during the blotting procedure despite the relatively high shear rates applied. In Figure 7C,D, a typical network caused by branched micelles is observed. Both micrographs show a number of three-way connections (black arrows). In addition, Figure 7D shows an increasing number of black dots in the background. This pattern is a consequence of freezing the highly concentrated salt solution (12 wt %). The results from the cryo-TEM study are in good agreement with the predictions from the steady shear rheology in which the decrease in viscosity was attributed to be a shift from linear wormlike micelles to branch wormlike micelles.

Conclusions

The rheological behavior of EHAC solutions strongly depends on salt concentration, surfactant concentration, and temperature. Depending on these variables, shear banding can be observed in this system. However, more studies are required to understand this phenomenon. The low-shear viscosity goes through a maximum with increasing salt concentration. The presence of the electrolyte screens the interactions between micelles, thus promoting uniaxial growth. Additionally, the decrease in viscosity with temperature follows an Arrhenius type behavior and is related to the decrease in wormlike micellar length. SANS experiments show that the salt-free solution forms strong interacting spherical micelles with an inner radius and an outer radius of $\sim$30 and $\sim$35 Å, respectively. Upon the addition of salt the structure peak gradually disappears and a transition from spherical micelles to wormlike micelles occurs. The wormlike micelles formed have a cross-sectional radius of gyration of $\sim$21 Å. A direct visualization of this evolution was observed from the cryo-TEM images. Spherical micelles were detected in the salt-free solutions and a multiconnected network with three-way connections was observed upon addition of 6 wt % KCl to the system. Thus, the maxima in the low-shear viscosity can be rationalized in terms of a transition from linear to branched wormlike micelles. Finally, the experimental techniques used in this study are complementary with each other, allowing a good understanding of the strong rheological response of EHAC solutions.

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