Dynamic Viscoelasticity of Gelling and Nongelling Aqueous Mixtures of Ethyl(hydroxyethyl)cellulose and an Ionic Surfactant

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ABSTRACT: Oscillatory shear experiments have been carried out over an extended temperature range (10−45 °C) on thermoreversible gelling and nongelling aqueous systems of ethyl(hydroxyethyl)cellulose (EHEC) of different polymer concentrations in the presence of various amounts of sodium dodecyl sulfate (SDS). At moderate ratios (r) of SDS/EHEC, the semidilute systems form gels at elevated temperatures, whereas no temperature-induced gels are formed at high values of r in this temperature region. The gel point temperature depends on the polymer/surfactant composition, similar to the cloud point. It is shown that phase separation and gelation are phenomena that are closely related. At the gel temperature, a power law frequency dependence of the dynamic moduli ($G' \sim G'' \sim \omega^n$) was constantly observed. Depending on the composition of the system, the viscoelastic exponent assumes values in the approximate range 0.1−0.7. This finding indicates that the structure of the incipient gel is strongly influenced by the concentrations of polymer and surfactant. The dynamic viscosity results suggest a strengthening of the association network at moderate values of r, while a gradual disruption of the network occurs at high levels of SDS addition. A temperature increase of semidilute EHEC solutions at moderate values of r gives rise to a strengthening of the network, whereas a temperature-induced weakening of the network structure is found at higher values of r.

Introduction

During the last years, the synergism of surfactants and polymers in aqueous solution has attracted much interest in fundamental and applied research. The interest of this topic is driven by the numerous industrial applications of water-borne fluids incorporating mixtures of polymers and surfactants. This type of systems is found in fluids for enhanced oil recovery, paints, food preparations, cosmetic formulations, and pharmaceutical compositions.

The aggregation of surfactants and cellulose ethers continues to be of special interest due to the industrial importance of this class of polymers. Several cellulose derivatives, such as the ethyl(hydroxyethyl)cellulose (EHEC) considered in this study, are characterized by mixed hydrophobic and hydrophilic structural units. Moreover, these structural elements are normally unevenly distributed along the polymer backbone and the substituents may consist of shorter or longer chains, giving rise to a varying degree of hydrophobicity. The interaction of this complex structure with an ionic surfactant can give this system extraordinary properties.[1−12] The binding of the surfactant to the polymer will give rise to the formation of micellar-type aggregates involving substituents from one or more EHEC chains. In semidilute solutions of EHEC, the surfactant clusters act either as junctions or strengthen already-existing connections between segments on different polymer molecules. This surfactant-promoted interpolymer interaction induces a viscosity enhancement that increases with increasing polymer concentration. These systems usually form thermoreversible gels at elevated temperatures. This phenomenon has been attributed[13] to the increased hydrophobicity of EHEC at higher temperatures, resulting in stronger polymer−polymer interactions. At higher levels of surfactant additions, the viscosity decreases strongly and it has been argued that this effect is due to the fact that additional surfactant aggregates are available for the “solubilization”[12] of the polymer-bound hydrophobes. As a result, the average number of bound hydrophobes per surfactant aggregate will decrease, thereby reducing the number of effective micellar-like cross-links. This leads to a gradual breakdown of the network structure.

From dynamic light-scattering[4,14] and rheological[4,8,15] measurements it is well-established that aqueous solutions of certain EHEC samples in the presence of moderate concentrations of the anionic surfactant sodium dodecyl sulfate (SDS) exhibit a thermoreversible sol−gel transition in the semidilute regime (ca. 1 wt % polymer), where the polymer molecules overlap each other. Upon heating, this type of system undergoes a transformation from a moderately viscous solution to a clear and stiff gel. As indicated above, the ability to form gels or to induce a viscosification effect in EHEC−ionic surfactant systems depend on the ratio of polymer concentration to surfactant addition and on the temperature of measurement.

In the present study, we have carried out oscillatory shear measurements on aqueous EHEC−SDS systems over a broad temperature range at different polymer concentrations and at various levels of surfactant addition. The aim of this work is to scrutinize how the rheological features are affected by the polymer−surfactant composition and temperature. The interplay between these factors is important to gain a thorough understanding of the gelation process and insight into the factors that strengthen or weaken the polymer network.

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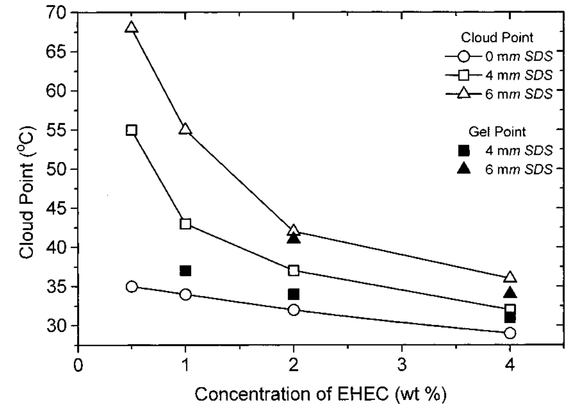

Figure 1. Effects of EHEC concentration and SDS addition on the cloud point (open symbols) and the gel point temperature (solid symbols).

Experimental Section

Materials and Sample Preparation. A sample of EHEC, designated Bermocoll DVT 89017, with a number average molecular weight (M_n) of approximately 80 000 and degrees of substitution of ethyl and hydroxyethyl groups of $DS_{ethyl} = 1.9$ and $MS_{EO} = 1.3$, respectively, was obtained from Akzo Nobel Surface Chemistry AB, Stenungsund, Sweden. The polymer is polydisperse with a polydispersity index (M_w/M_n) of about 2. The values of DS and MS correspond to the average numbers of ethyl and hydroxyethyl groups, respectively, per anhydroglucose unit of the polymer. EHEC dissolved in water exhibits a lower consolute solution temperature (LCST) (demixing upon heating). The cloud points (CP) of aqueous EHEC solutions without surfactant decrease as the polymer concentration increases (see Figure 1). The cloud points were visually taken by eye as the temperature where samples are transformed from perfectly clear to turbid solutions. The values of M_n, MS, and DS were all given by the manufacturer. The anionic surfactant SDS was purchased from Fluka and was used as received.

Dilute EHEC solutions were dialyzed against pure water for several days to remove salt rests (impurity from the manufacturing) and were thereafter freeze-dried. As a dialyzing membrane, regenerated cellulose with a molecular weight cutoff of 8000 (Spectrum Medical Industries) was used. After freeze-drying (and drying at an elevated temperature prior to use), the polymer was redissolved in aqueous media with the desired SDS concentrations. Samples were prepared by weighing the components, and the solutions were homogenized by stirring at room temperature for several days.

Oscillatory Shear Experiments. Oscillatory shear measurements were conducted in a Bohlin VOR rheometer system using, depending on the viscosity of the sample, a double-gap concentric cylinder, an ordinary concentric cylinder geometry, or a cone-and-plate geometry, with a cone angle of 5° and a diameter of 30 mm at a strain less than 0.02. The double-gap device is applicable for low-viscosity liquids. Since measurements were performed at elevated temperatures, a layer of silicone oil was always added to the sample to avoid evaporation of the solvent. The values of the strain amplitude were checked to ensure that all measurements were carried out within the linear viscoelastic regime, where the dynamic storage modulus (G') and loss modulus (G'') are independent of the strain amplitude. The oscillating sweep measurements were carried out in the approximate frequency (ω) domain 0.01−3 Hz. The rheometer is equipped with a temperature control unit that was calibrated to give a temperature in the sample chamber within 0.1 °C of the set value. At each temperature, the sample was allowed to equilibrate for about 1 h before measurements were commenced. In these experiments, no disturbing hysteresis effects were observed.

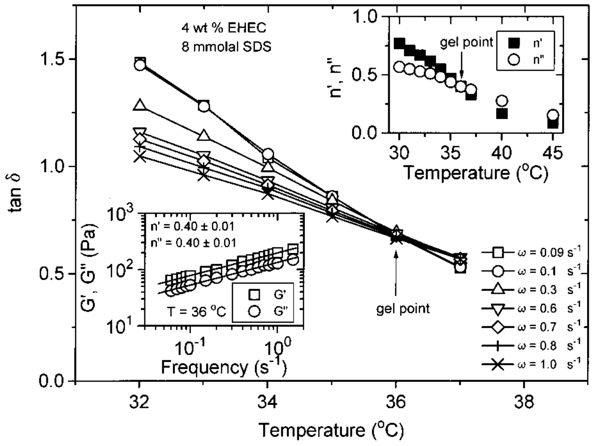

Figure 2. Illustration of methods for the determination of the gel point. Viscoelastic loss tangent as a function of temperature for the system and frequencies indicated. The upper inset plot shows changes of the apparent exponents n' for the storage and n'' for the loss moduli during the course of gelation. The lower inset plot shows the power law behavior of the dynamic moduli at the gel point temperature.

Results and Discussion

Gelling Systems. We will now discuss some characteristic properties of gelling EHEC/SDS systems. The gel point of a thermoreversible gel can be determined by observation of a frequency-independent value[16] of tan δ ($=G''/G'$) obtained from a multifrequency plot of tan δ versus temperature (see Figure 2). An alternative method[17] to determine the gel point is to plot against temperature the "apparent" viscoelastic exponents n' and n'' ($G' \sim \omega^{n'}$, $G'' \sim \omega^{n''}$) obtained from the frequency dependence of G' and G'' at each temperature of measurement and observing a crossover where $n' = n'' = n$ (see the upper inset of Figure 2). It is evident from Figure 2 that these methods yield the same gelation temperature for the considered gelling system (4 wt % solution of EHEC in the presence of 8 m*m* SDS). These two methods always produced the same gelation temperature for the systems considered in this study. The general feature observed for all the gelling EHEC−SDS systems is that the loss tangent, tan δ, decreases during the gel formation, indicating that the solutions become more and more elastic. At the gel point temperature, the G' and G'' curves become parallel and power laws in frequency are observed over a frequency domain of more than two decades (see the lower inset of Figure 2).

A typical illustration of the frequency dependence of G' and G'' at different stages during the thermoreversible gelation process is depicted in Figure 3. The data are shifted horizontally by a factor of B (see the insets in Figure 3) to avoid overlap. The general trend for all systems is that at temperatures well-below the gel temperature, G' is smaller than G'' at low frequencies and a liquid-type behavior is predominant. At the gel temperature, the G' and G'' curves become parallel and power laws in frequency are observed over the considered frequency domain. At temperatures above the gel temperature, G' increases rapidly and becomes much larger than G''. This behavior is characteristic of the solidlike state that evolves above the gel point.

Before we discuss how the gel point and other characteristic properties of the incipient gel are influenced by surfactant addition and polymer concentration, it may be helpful to describe a scenario where these

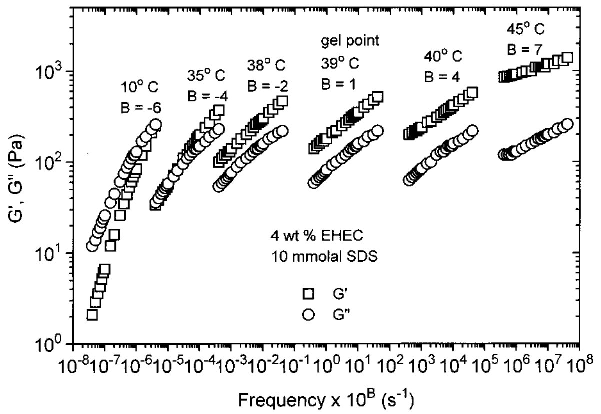

Figure 3. Frequency dependences of the storage modulus G' and the loss modulus G'' at different stages of the gel-forming process for the system indicated. The curves have been shifted horizontally by a factor B of the value listed in the inset.

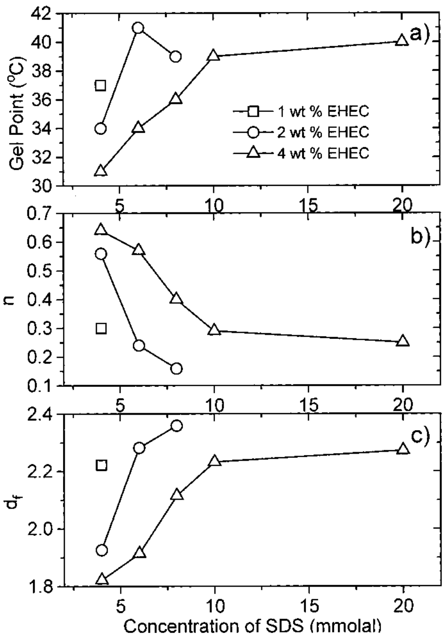

Figure 4. Effects of polymer concentration and surfactant addition on the gel point temperature (a), on the viscoelastic exponent (b), and on the fractal dimension d_f (c) (calculated from eq 1).

features can be rationalized. A model for the description of temperature-induced gelation in EHEC–ionic surfactant systems has recently been suggested by Cabane et al.[7] In EHEC solutions without surfactant, a temperature raise induces a macroscopic phase separation of the solution into a polymer-rich phase and an excess aqueous phase. As was demonstrated above (see Figure 1), the cloud point temperature decreases with increasing polymer concentration. Upon addition of an ionic surfactant (e.g., SDS) to the EHEC solution, adsorption of the surfactant to the polymer chains occurs and the phase-separation behavior of EHEC is modified because the surfactant causes fragmentation of the large domains of the polymer-rich phase into microscopic "lumps"[7] (bundles of associating chains) which are stabilized by the bound ionic surfactant on the surfaces of these "lumps". Each "lump" is formed by the loose association of polymer chains belonging to different polymer molecules, and the adsorption of the ionic surfactant endows a polyelectrolyte character of the "lumps". We may note that the cloud points for the considered EHEC concentrations are shifted toward higher values as the surfactant concentration increases (see Figure 1), implying that the thermodynamic conditions of the systems are improved.

Small angle neutron-scattering experiments[7,18] on aqueous EHEC–ionic surfactant systems have shown that the "lump" sizes increase at elevated temperatures and decrease with increasing surfactant concentration. The picture that emerges is that the size and the growth of the lumps are governed by the interplay between temperature, surfactant addition, and polymer concentration. For instance, in a semidilute solution of EHEC with a moderate level of surfactant addition, a temperature rise is expected to favor the formation of lumps. The permanent connectivity of EHEC gels is provided by the growing lumps, and the swelling properties are generated by the electrostatic repulsions of the ionic surfactant. To have both swelling and connectivity of the gel, we need to be close to phase separation (see the discussion below) (i.e., to have balance between repulsive (swelling) and attractive (connecting) forces).

The effects of surfactant addition and EHEC concentration on the gelation point are displayed in Figure 4a. The general trend is that the gelation temperature rises with decreasing polymer concentration (at a fixed surfactant addition) and with increasing surfactant concentration (for a constant polymer concentration). At 1 wt % polymer an incipient gel evolves at 4 m*m* SDS, while at higher levels of surfactant addition no temperature-induced gel is formed in the investigated temperature region because the sizes of the lumps are not sufficiently large to provide the necessary connectivity of the gel network. For the highest polymer concentration (4 wt %), on the other hand, the connectivity needed for gelation lasts up to an SDS concentration of 20 m*m*. The features observed in Figure 4a can be rationalized in the following way. The kinship between phase separation and gelation has been recognized in a number of studies[19–22] on thermoreversible gels. It was argued that thermoreversible gelation and phase separation are phenomena which are closely correlated to each other. In light of this, we expect the gelation temperature to decrease with increasing EHEC concentration at a fixed level of SDS addition (cf. the trend for the cloud point in Figure 1). At a given polymer concentration, the surmise is that the gel point rises as the surfactant concentration increases because the thermodynamic conditions of the system are gradually improved (i.e., the cloud point is shifted toward higher values). As a result, a higher temperature is needed to establish the connectivity necessary for gel formation. It is shown in Figure 1 (see the solid symbols) that phase separation and gelation follow each other and that the gel temperature is lower than the corresponding cloud point temperature. It has been argued[22] from a Monte Carlo simulation model that due to the coexistence of phase separation and gelation, the cross-linking may arrest the phase-separation process.

To fulfill the connectivity condition for gelation, it seems to be necessary to be in the semidilute concentration regime, where the polymer chains overlap each other and form a transient network. This is probably the reason why the 0.5 wt % EHEC solution in the presence of SDS does not form a gel at elevated temperatures. Besides being in the semidilute polymer concentration range, it is also crucial for the gelation process that the level of surfactant addition is above the critical aggregation concentration (cac), where the onset of surfactant binding to the polymer occurs. Depending on the temperature, values of the cac in the range 1−2 mM have been reported[23] for the present EHEC/SDS system. At this stage, it may be instructive to discuss the gelation characteristics of the present systems in terms of the SDS-to-EHEC concentration ratio $r = C_{\mathrm{SDS}}/C_{\mathrm{EHEC}}$ (the concentrations for both components are expressed in weight fraction). The results from the systems considered in this study indicate that thermoreversible gels are formed in the approximate range $0.02 < r < 0.1$. At values below 0.02, the solutions become turbid (macroscopic phase separation) at elevated temperatures, while at values of r above 0.1, the connectivity condition for gelation is not fulfilled. These findings reveal that the ratio between surfactant addition and polymer concentration is crucial for the ability of the system to form a thermoreversible gel.

The present oscillatory shear experiments have been performed in the temperature interval 10−45 °C. At higher temperatures, it was difficult with the present equipment to obtain reproducible results because disturbing evaporation effects. However, in connection with the determination of the cloud points, we observed some interesting effects. For instance, for the 1 wt % EHEC sample in the presence of 6 m*m* SDS, a gellike state evolved at a temperature around 53 °C. We are now trying to develop a procedure so that the rheological features of these EHEC−SDS systems can be examined at much higher temperatures.

Figure 4b shows how the value of the relaxation exponent n varies as the polymer and surfactant concentrations are changed. We can see that at a given polymer concentration, the value of n falls off with an increasing level of surfactant addition, while for a fixed surfactant concentration n seems to assume higher values as the polymer concentration increases. These results suggest that the structure of the incipient gel depends on the polymer−surfactant composition.

In the interpretation of the relaxation exponent, two main theoretical approaches, which take into account the fractal geometry of polymer clusters and their intrinsic irregular structure, have been developed. On the basis of a suggested[24,25] isomorphism between the complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors, a value of $n = 0.72$ was predicted. In the other approach,[26] the Rouse model, which assumes no hydrodynamic interaction between polydisperse polymeric clusters, together with percolation statistics yielded a value of $n = 2/3$. Since these values are close to each other, dynamic rheological experiments do not allow one to distinguish between these predictions. Several experimental investigations on various gelling systems, such as polyurethanes[27] ($n = 0.69 \pm 0.04$), epoxy resins[26] ($n = 0.70 \pm 0.05$), polyesters[28] ($n = 0.69 \pm 0.02$), tetraethoxysilane[29] ($n = 0.72 \pm 0.02$), silyl-terminated poly(oxypropylene)[30,31] ($n = 0.66 \pm 0.02$), and the physical gels of gelatin[32] ($n = 0.69 \pm 0.02$) and of calcium pectate[33] ($n = 0.71 \pm 0.02$), seem all to support these models with values of n around 0.7. However, a number of oscillatory shear studies[3,8,16,34−43] on incipient gels of various natures indicate that n is not a constant but takes values in the range $0 < n < 1$, depending on the structure of the species in the gelation process, the stoichiometric ratio, the gel preparation method, and also polymer molecular weight and concentration.

To rationalize values of n in the whole physically accessible range ($0 < n < 1$), Muthukumar developed a theoretical model[44] in which it is assumed that variations in the strand length between cross-linking points of the incipient gel network give rise to changes of the excluded volume interactions. The surmise is that increasing strand length will enhance the excluded volume effect. To account for this effect, Muthukumar suggested that if the excluded volume interaction is fully screened, the relaxation exponent for a polydisperse system can be expressed as

$$n = \frac{d(d + 2 - 2d_{\mathrm{f}})}{2(d + 2 - d_{\mathrm{f}})} \tag{1}$$

where d ($d = 3$) is the spatial dimension and d_{f} is the fractal dimension which relates the mass of a molecular cluster to its radius of gyration by $R^{d_{\mathrm{f}}} \sim M$. In the framework of eq 1, all values of the relaxation exponent $0 < n < 1$ are possible for a fractal in the physically realizable domain $1 \leq d_{\mathrm{f}} \leq 3$.

The effects of the polymer concentration and the addition of surfactant on the fractal dimension, calculated with the aid of eq 1, of incipient gels of EHEC are depicted in Figure 4c. The results show that the fractal dimension decreases with increasing polymer concentration at a constant level of surfactant addition. The same trend in d_{f} is also observed with decreasing SDS concentration at a fixed EHEC concentration. These changes in polymer and surfactant concentration are both expected to promote the formation of large lumps of associating polymer chains in the incipient gel networks. The conjecture is that the formation of large lumps gives rise to a more heterogeneous network than those formed under lower EHEC concentrations or higher levels of surfactant addition. The enhanced spatial inhomogeneity in the growth of a strongly associating gel network, consisting of large lumps, may lead to a more “open” network structure[37,44,45] (i.e., the fractal dimension decreases).

Effects of Temperature and Surfactant and Polymer Concentrations on the Dynamic Viscosity. In this study the dynamic viscosity ($\eta' = G''/\omega$) will be used in the characterization of the effects of temperature and surfactant and polymer concentrations on the viscoelastic properties of EHEC/SDS systems.

The effects of temperature and polymer and surfactant concentrations on the dynamic viscosity are depicted in Figure 5a. The general trend is that η' passes through a maximum, which is shifted toward higher surfactant concentrations as the polymer concentration increases. The rise of η' at moderate surfactant additions is due to a reinforcement of the temporary association network. It may be instructive to discuss this effect in the framework of a modified version[18] of the earlier model of Cabane et al.[7] On the basis of small angle neutron-scattering experiments on semidilute aqueous EHEC−SDS systems, it has recently been argued[18] that the structure of these solutions can be described by a mesh of overlapping polymer + surfactant “necklaces” coexisting with lumps. The magnitude of these two structures varies according to the SDS/EHEC ratio and to the temperature. The formation of lumps is favored at low values of r and high temperatures, while high ratios and low temperatures promote

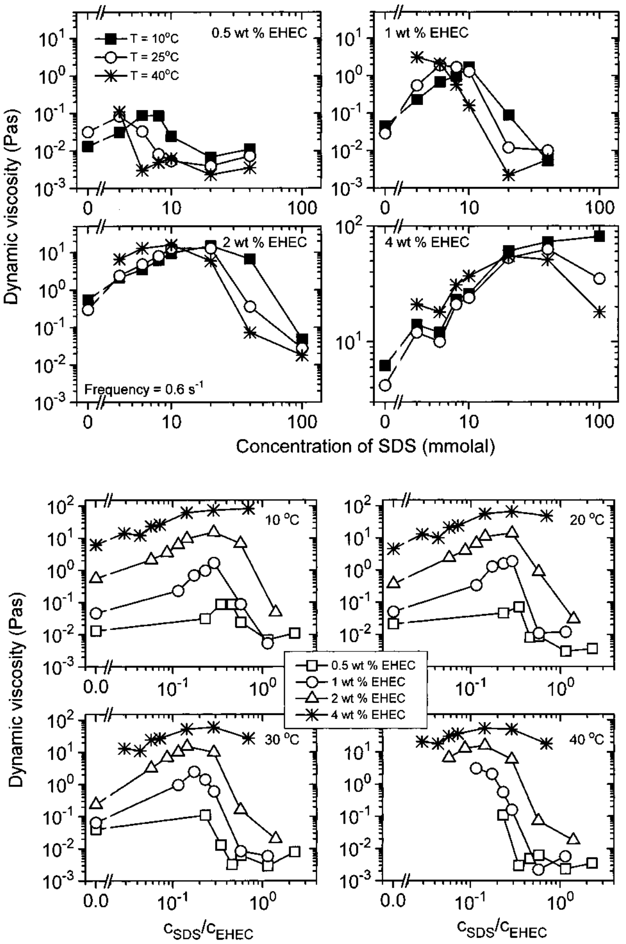

Figure 5. Effects of polymer concentration and surfactant addition on the dynamic viscosity (0.6 Hz) at the temperatures indicated (a). SDS-EHEC composition dependence of the dynamic viscosity at the polymer concentrations and temperatures indicated (b).

the evolution of necklaces (made of SDS micelles collected by EHEC molecules). In a semidilute aqueous solution of EHEC in the presence of SDS, the delicate interplay between necklaces and lumps (the lumps act as cross-links for the macromolecules of the mesh) gives rise to an association network which attains its optimum strength at a certain surfactant level $C_{\mathrm{SDS,max}}$, or at a certain surfactant-to-polymer ratio. The maxima of the dynamic viscosity may be regarded as estimates of $C_{\mathrm{SDS,max}}$. As observed in Figure 5a, the value of this parameter varies with the EHEC content. At SDS addition above $C_{\mathrm{SDS,max}}$, the lumps will gradually break down and the structure of the solutions can be viewed as a mesh of overlapping necklaces. In this process, the number of effective micellar-type cross-links is reduced. As a result, η' falls off with increasing surfactant concentration and a gradual disruption of the network occurs. At very high surfactant concentrations, we have a solution consisting of separated necklaces with strong repulsive correlation between them.

A close inspection of the data in Figure 5a reveals that the maximum of η' is shifted toward lower SDS concentrations with increasing temperature; this tendency is especially conspicuous at 4 wt % EHEC. We may also note that the strongest temperature effect of η' is observed at approximate surfactant concentrations of 8, 20, 40, and 100 m*m* for the EHEC concentrations of 0.5, 1, 2, and 4 wt %, respectively. This corresponds to a surfactant-to-polymer ratio of $r \approx 0.5$, which represents a stoichiometric composition where the binding of the surfactant to the polymer is saturated.[18] The marked decrease of η' at this condition upon rising temperature suggests a temperature-induced weakening of the network. At this fairly high value of r, the structure of these solutions, at least for the three highest EHEC concentrations, can be described as a mesh of overlapping necklaces. These findings indicate that the binding of these necklaces to each other is weaker at elevated temperatures. At still higher levels of surfactant addition, it seems that the effect of temperature on η' practically disappears (this feature is evident at high surfactant concentrations for the 1 and 2 wt % EHEC samples in Figure 5a). At this stage, the networks are disrupted and the solutions can be viewed as consisting of individual necklaces.

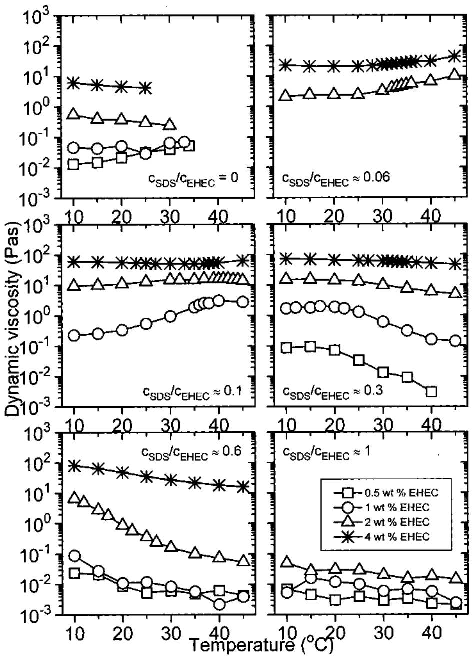

Figure 6. Temperature dependence of the dynamic viscosity (0.6 Hz) at the surfactant-polymer ratios and EHEC concentrations indicated.

In Figure 5b, η' (at a constant frequency of 0.6 Hz) is plotted as a function of $r = C_{\mathrm{SDS}}/C_{\mathrm{EHEC}}$ at different polymer content and temperatures. In this type of normalized plot, the maxima of the dynamic viscosity are located at practically the same value of r independent of the polymer concentration, but η' assumes higher values when the polymer concentration is increased (the strength of the network increases). This phenomenon is not unexpected because of enhanced entanglement effects at higher polymer concentrations. Furthermore, we can see that the maxima are shifted toward lower values of r as the temperature is raised. This may be due to the fact that the value of cac decreases with increasing temperature.[9,23,46] It seems that the maximum of η' becomes more shallow with increasing EHEC concentration. These results suggest that the ratio r is an important parameter in the analysis of rheological properties of EHEC−surfactant systems.

Figure 6 shows the effect of temperature on the dynamic viscosity for different polymer−surfactant compositions. The general picture that emerges from these results is that a temperature increase induces a strengthening (increasing values of η') of the network (the lumps grow at the expense of the mesh) at low values of r, while at high values of r a temperature rise leads to a weakening (decreasing values of η') of the network. For instance, to observe a temperature-induced breakdown (in the considered temperature range) of the network formed at the highest polymer concentration (4 wt %), a rather high level of surfactant addition ($r \geq 0.3$) is needed. The intricate interplay between the concentration of EHEC and the temperature appears clearly in the case of $r \approx 0.3$. At this stage, we can see that at the highest polymer concentration, η' is only slightly affected upon a temperature rise, while a gradually stronger decrease of η' with increasing temperature is observed as the polymer concentration decreases. We may also note that η' always displays higher values with increasing polymer concentration (enhanced entanglement effects). Furthermore, at low temperatures the changes of η' with polymer concentration are of the same order of magnitude as those observed under the corresponding conditions in the absence of SDS. This suggests that, at low temperatures, the polymer concentration effect controls the behavior of η' even at quite high levels of surfactant addition. However, at the highest ratio ($r \approx 1$), a fairly weak temperature and concentration dependence of η' can be traced, and the values of η' are consistently lower than the corresponding ones for the EHEC solutions without surfactant. The low values of η' observed at high levels of surfactant addition indicate that the polymer networks are more or less disrupted at these conditions.

Summary and Conclusions

In this work, oscillatory shear experiments were carried out at different temperatures on gelling and nongelling aqueous systems of EHEC of different concentrations in the presence of various amounts of SDS. We have shown that these systems exhibit complex rheological features. Most of the findings can be rationalized in the framework of a model where the structure of the systems can be visualized as a mesh of overlapping necklaces made of SDS micelles collected by EHEC chains, in coexistence with lumps of associated EHEC macromolecules. The formation of lumps is promoted at low SDS/EHEC ratios r at elevated temperatures, while at low temperatures and high levels of surfactant addition the lumps are disrupted and the structure of the solutions can be described as a mesh of more or less overlapping necklaces. The main results can be summarized in the following way: (1) The gel point depends on the polymer−surfactant composition similar to the cloud point. At a fixed SDS addition, the gel point temperature decreases with increasing concentration of EHEC, while at a constant polymer concentration the gel point rises with increasing levels of surfactant addition. The gel points of the systems are below their corresponding cloud points, but gelation and phase separation are found to be correlated to each other. (2) For the thermoreversible gelling systems, it is observed for the incipient gels that G' parallels G'' over an extended frequency domain and the dynamic moduli can be described by power laws $G' \sim G'' \sim \omega^n$. The values of n are located in the approximate range 0.1−0.7. The value of the viscoelastic exponent depends on both polymer and surfactant concentrations. On the basis of a fractal model of Muthukumar for gelation, these results suggest that the structure of the incipient gel is strongly influenced by the polymer−surfactant composition. (3) The effects of temperature and surfactant and polymer concentrations on the dynamic viscosity have been examined systematically. The dynamic viscosity η' passes through a maximum at a certain surfactant/polymer ratio. A strengthening of the association network is observed at moderate values of this ratio, while a gradual disruption of the network occurs at high levels of surfactant addition. Probably due to a temperature-dependent critical aggregation concentration, this ratio is shifted toward lower values with increasing temperature. (4) At moderate values of r in the semidilute polymer concentration regime, a temperature increase gives rise to a strengthening of the polymer network, whereas a temperature-induced weakening of the structure is observed at higher values of r.

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References and Notes

(1) Carlsson, A. Ph.D. Dissertation, Lund University, Lund, Sweden, 1989.
(2) Piculell, L.; Lindman, B. *Adv. Colloid Interface Sci.* **1992**, *41*, 149.
(3) Nyström, B.; Walderhaug, H.; Hansen, F. K.; Lindman, B. *Langmuir* **1995**, *11*, 750.
(4) Nyström, B.; Lindman, B. *Macromolecules* **1995**, *28*, 967.
(5) Wang, G.; Olofsson, G. *J. Phys. Chem.* **1995**, *99*, 5588.
(6) Bloor, D. M.; Wan-Yunus, W. M. Z.; Wan-Badhi, W. A.; Li, Y.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **1995**, *11*, 3395.
(7) Cabane, B.; Lindell, K.; Engström, S.; Lindman, B. *Macromolecules* **1996**, *29*, 3188.
(8) Nyström, B.; Kjøniksen, A.-L.; Lindman, B. *Langmuir* **1996**, *12*, 3233.
(9) Medeiros, G. M. M.; Costa, S. M. B. *Colloids Surf. A: Physicochem. Eng. Aspects* **1996**, *119*, 141.
(10) Hansson, P.; Lindman, B. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 604.
(11) Holmberg, C.; Nilsson, S.; Sundelöf, L.-O. *Langmuir* **1997**, *13*, 1392.
(12) Wang, G.; Lindell, K.; Olofsson, G. *Macromolecules* **1997**, *30*, 105.
(13) Lindman, B.; Carlsson, A.; Karlström, G.; Malmsten, M. *Adv. Colloid Interface Sci.* **1990**, *32*, 183.
(14) Nyström, B.; Roots, J.; Carlsson, A.; Lindman, B. *Polymer* **1992**, *33*, 2875.
(15) Carlsson, A.; Karlström, G.; Lindman, B. *Colloids Surf.* **1990**, *47*, 147.
(16) Winter, H. H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367.
(17) Hodgson, D. F.; Amis, E. J. *J. Non-Cryst. Solids* **1991**, *131−133*, 913.
(18) Lindell, K.; Cabane, B. Submitted for publication.
(19) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943.
(20) Tanaka, F. *Adv. Colloid Interface Sci.* **1996**, *63*, 23.
(21) Tanaka, F.; Ishida, M. *Macromolecules* **1996**, *29*, 7571.
(22) Liu, Y.; Pandey, R. B. *J. Chem. Phys.* **1996**, *105*, 825.
(23) Kamenka, N.; Burgaud, I.; Zana, R.; Lindman, B. *J. Phys. Chem.* **1994**, *98*, 6785.
(24) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(25) Alexander, S. *J. Phys. (Paris)* **1984**, *45*, 1939.
(26) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 2620; *Phys. Rev. A* **1989**, *39*, 1325.
(27) Durand, D.; Delsanti, M.; Adam, M.; Luck, J. M. *Europhys. Lett.* **1987**, *3*, 297.
(28) Rubinstein, M.; Colby, R. H.; Gillmor, J. R. *Am. Chem. Soc., Polym. Prepr.* **1989**, *30*, 81.
(29) Hodgson, D. F.; Amis, E. J. *Macromolecules* **1990**, *23*, 2512.
(30) Koike, A.; Nemoto, N.; Takahashi, M.; Osaki, K. *Polymer* **1994**, *35*, 3005.
(31) Takahashi, M.; Yokoyama, K.; Masuda, T.; Takigawa, T. *J. Chem. Phys.* **1994**, *101*, 798.

(32) Hsu, S.; Jamieson, A. M. *Polymer* **1993**, *34*, 2602.
(33) Axelos, M. A. V.; Kolb, M. *Phys. Rev. Lett.* **1990**, *64*, 1457; *Macromol. Chem., Macromol. Symp.* **1992**, *45*, 23.
(34) Chambon, F.; Winter, H. H. *J. Rheol.* **1987**, *31*, 683.
(35) Chambon, F.; Petrovic, Z. S.; MacKnight, W. J.; Winter, H. H. *Macromolecules* **1986**, *19*, 2146.
(36) Vallés, E. M.; Carella, J. M.; Winter, H. H.; Baumgaertel, M. *Rheol. Acta* **1990**, *29*, 535.
(37) Scanlan, J. C.; Winter, H. H. *Macromolecules* **1991**, *24*, 47.
(38) Muller, R.; Gérard, E.; Dugand, P.; Rempp, P.; Gnanou, Y. *Macromolecules* **1991**, *24*, 1321.
(39) Müller, O.; Gaub, H. E.; Bärmann, M.; Sackmann, E. *Macromolecules* **1991**, *24*, 3111.
(40) Cuvelier, G.; Launay, B. *Macromol. Chem., Macromol. Symp.* **1990**, *40*, 23.
(41) Lin, Y. G.; Mallin, D. T.; Chien, J. C. W.; Winter, H. H. *Macromolecules* **1991**, *24*, 850.
(42) Carnali, J. O. *Rheol. Acta* **1992**, *31*, 399.
(43) Kjøniksen, A.-L.; Nyström, B. *Macromolecules* **1996**, *29*, 5215.
(44) Muthukumar, M. *J. Chem. Phys.* **1985**, *83*, 3161.
(45) Izuka, A.; Winter, H. H.; Hashimoto, T. *Macromolecules* **1992**, *25*, 2422.
(46) Evertsson, H.; Nilsson, S.; Holmberg, C.; Sundelöf, L.-O. *Langmuir* **1996**, *12*, 5781.

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