

Conformation of Poly(ethylene oxide) in Polymer–Surfactant Aggregates

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Received: September 11, 2003; In Final Form: December 19, 2003

The influence of sodium dodecyl sulfate (SDS) on the conformation of poly(ethylene oxide) (PEO) in water is studied using viscosity measurements and small-angle neutron scattering (SANS). The behavior, as a function of surfactant concentration above the critical aggregation concentration (CAC), can be described in terms of two separate regimes: an initial regime in which micelles are attached to the coils but are noninteracting and a second regime in which there is interaction between the attached micelles. The latter is characterized by a strong increase in viscosity and other features similar to polyelectrolytes. On the contrary, in the initial regime, our results suggest a slight decrease in coil size under ambient conditions and a much more significant decrease at elevated temperatures. The cloud point of PEO in water exhibits a minimum as a function of surfactant concentration. We believe the minimum in the cloud point corresponds to a crossover from the noninteracting to the interacting regime.

Introduction

The conformation of poly(ethylene oxide) (PEO) in aqueous solutions containing a mixture of PEO and surfactant has been studied by a number of investigators.^{1–7} For example, a typical result for the variation of viscosity of a semidilute solution of high molecular weight PEO, as function of the concentration of sodium dodecyl sulfate (SDS) in the presence of a small amount of 1–1 electrolyte (sodium chloride), is shown in Figure 1. The dominant feature is an increase in viscosity with an increase in SDS concentration, that is readily explained on the basis of electrostatic repulsions between attached micelles resulting in expansion of individual coils. The increase in viscosity (region B) continues until the coils are saturated with the surfactant.⁸ Beyond this point, one observes a plateau in viscosity (region C) until the onset of a sphere-to-rod transition in the SDS micelles. Entanglement of rodlike micelles results in a further increase in viscosity (region D).⁹ Our interest here is in region A, where one observes a very small decrease in viscosity just beyond the onset of self-assembly or the critical aggregation concentration (CAC). The decrease in viscosity in this regime has been reported previously in at least two publications,^{2,6} but there has been no satisfactory explanation of the phenomenon. In a separate neutron scattering study, Cabane and Duplessix¹⁰ noted that the PEO chain undergoes a slight compression when it adsorbs a small number of micelles—a result consistent with the rheological observations. However, recent theoretical studies^{11,12} indicate a stronger effect. They suggest a partial collapse of the polymer chain in the vicinity of the CAC. If this is true, we might expect much larger changes in coil size and viscosity.¹³

In this paper, we take a fresh look at the problem using both viscosity measurements and small-angle neutron scattering (SANS). We show that the initial conformational change above the CAC is a contraction of the polymer coil. The coil continues

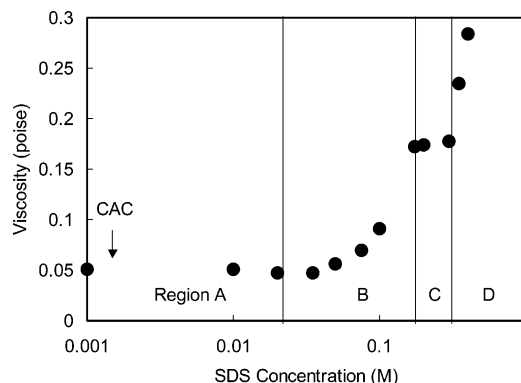


Figure 1. Viscosity as a function of SDS concentration for PEO in water ($M_w = 250\,000$, 1.15% w/v) in the presence of 0.02 M sodium chloride.

to contract as more and more micelles attach to it until the average distance between micelles is on the order of the electrical double layer thickness. The attachment of micelles in this regime results in a significant reduction in the cloud point of PEO in water. The latter exhibits a minimum as a function of surfactant concentration, which corresponds to the minimum in viscosity.

Experimental Section

Materials. Poly(ethylene oxide) (PEO) was purchased from Tosoh Corporation. Two different materials were used in the study: type SE-30 Lot No. RE-35 and type SE-8 Lot No. RE-31. The first sample had a weight-average molecular weight (M_w) of 250 000 and polydispersity (M_w/M_n) of 1.04, and the second one had M_w of 107 000 and polydispersity of 1.05. Sodium dodecyl sulfate was obtained from Eastman Kodak Company. Deuterium-labeled SDS (*d*-SDS) and deuterium oxide (D_2O) used in the SANS experiments were obtained from C/D/N Isotopes, Inc. and Cambridge Isotope Laboratories, Inc., respectively.

Methods. Viscosities of aqueous solutions containing a mixture of PEO and SDS were determined using a Carri-med

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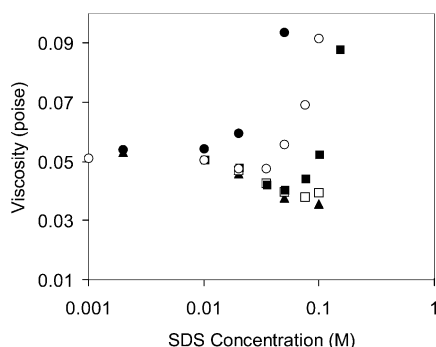


Figure 2. Viscosity as a function of SDS concentration for PEO in water ($M_w = 250\,000$, 1.15% w/v) and various levels of salt: no salt (filled circles); 0.02 M sodium chloride (open circles); 0.1 M (filled squares); 0.3 M (open squares); and 0.68 M (filled triangles).

CSL 100 controlled-stress rheometer equipped with a double concentric cylinder-measuring geometry. All samples exhibited Newtonian flow in the shear rate range 0–500 s^{-1} .

Small-angle neutron scattering measurements of solutions of PEO and deuterium-labeled SDS (*d*-SDS) were performed using the time-of-flight small-angle diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. A medium of pure D_2O was used to almost match the neutron scattering length density of *d*-SDS so that the observed scattering was mainly from the polymer.¹⁴ Details of the instrument setup and operation are described elsewhere.¹⁵ Sample quartz cells with a 2 mm path length were used. Data for intensity of scattering, $I(Q)$, for values of the scattering vector, Q , ranging from 0.008 to 0.2 \AA^{-1} were collected over 8 h. All measurements were done at 25 $^\circ\text{C}$. The data were treated according to standard methods used by Argonne National Laboratory and included calibration, corrections for transmission and sample thickness, and subtraction of scattering from the solvent.

Cloud points were determined by visually observing the onset of turbidity as samples were heated in a water bath.¹⁶

The critical aggregation concentration (CAC) of SDS in the presence of PEO was determined from surface tension measurements at the air–water interface using the Wilhelmy plate technique. The method has been described in detail in a prior publication.¹⁷

Results and Discussion

Figure 2 shows the viscosity of a 1.15% w/v solution of PEO (type SE-30) as a function of the SDS concentration in the presence of different amounts of sodium chloride. It is clear that the decrease in viscosity is more pronounced at higher salt concentrations. Furthermore, the minimum in the curve shifts to higher SDS concentration at higher levels of salt. The latter is easily explained. If micelles are attached to polymer coils, the average distance between micelles has to be on the order of the electrical double layer thickness before the coils can expand. Because the electrical double layer thickness is reduced at higher salt concentrations, the micelles have to be closer and, consequently, there would be a greater number of micelles per coil at the onset of expansion. The results may be analyzed more quantitatively as follows. Let us denote by c_m the concentration of SDS corresponding to the minimum in the curves in Figure 2. The number of micelles attached to the coil at c_m should be proportional to $R_g^3/(R_m + \kappa^{-1})^3$ where R_g is the radius of gyration of the polymer coil, R_m is the radius of a micelle (approximately 20 \AA), and κ^{-1} is the electrical double layer thickness (see Figure 3). The latter is given by $\kappa^{-1} = (\epsilon k_B T /$

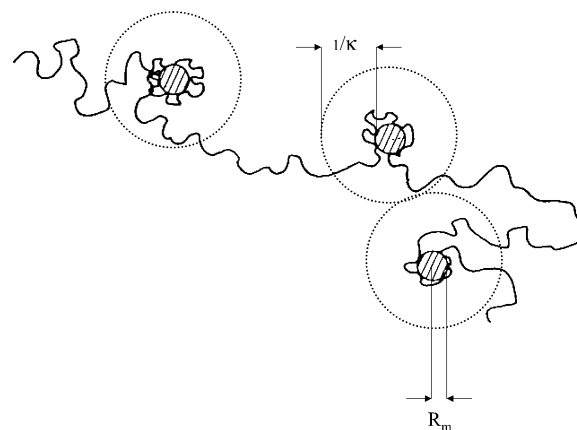


Figure 3. Bead and necklace model (adapted from ref 26).

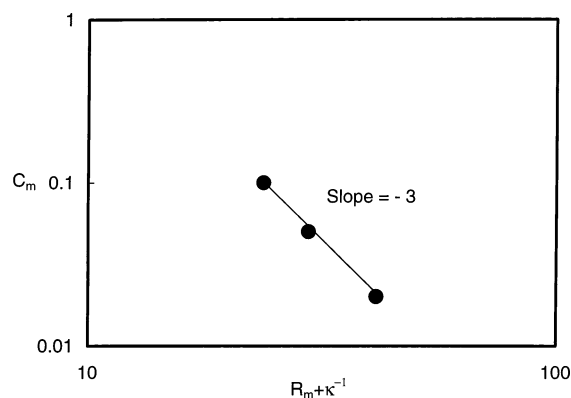


Figure 4. Relationship between the concentration of SDS (in moles per liter) at the minimum in viscosity and the electrical double layer thickness (in \AA).

$8\pi\mu e^2 v^2)^{1/2}$ where ϵ is the dielectric constant of the medium, μ is the number of ions per cm^3 at a distance from the surface of the micelle, e is the electronic charge, and v the valency of the electrolyte.¹⁸ Because the number of micelles attached to the coil is also proportional to $(c_m - \text{CAC})/N_{\text{Ag}} \approx c_m/N_{\text{Ag}}$ for $c_m \gg \text{CAC}$, where N_{Ag} is the mean aggregation number of the micelles, we have

$$c_m \sim R_g^3 N_{\text{Ag}} / (R_m + \kappa^{-1})^3 \quad (1)$$

If we assume that R_g is near constant in this regime and also that the size and aggregation number of polymer-bound micelles are relatively invariant with salt concentration, it follows from eq 1 that c_m should be roughly proportional to $(R_m + \kappa^{-1})^{-3}$. In other words, a plot of $\log c_m$ versus $\log(R_m + \kappa^{-1})$ should be a straight line with slope close to -3 . Figure 4 shows that this is the case.

Figure 5 shows the intensity of neutron scattering $I(Q)$ as a function of the scattering vector Q for solutions of PEO and SDS under contrast-match conditions for SDS (*d*-SDS in D_2O). The concentration and molecular weight of the polymer are the same as before. In the absence of the surfactant, one observes scattering typical of a semidilute solution of a high molecular weight polymer in a good solvent.¹⁹ With the 100 mM surfactant and in the absence of salt, one observes a “peak” that is characteristic of polyelectrolytes.²⁰ Segment density fluctuations are significantly suppressed at length scales larger than the correlation length in semidilute solutions. This should be contrasted with the behavior in the presence of both the 100 mM surfactant and 0.68 M sodium chloride. The composition

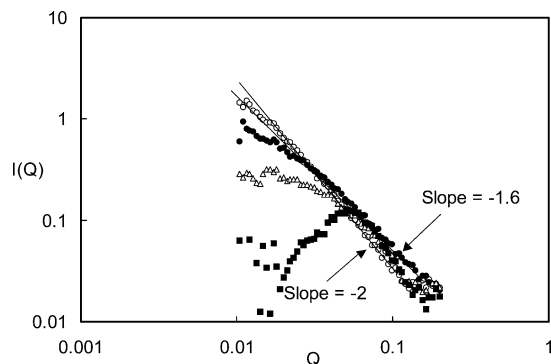


Figure 5. Intensity of neutron scattering as a function of the wave vector (in inverse Å) for mixtures of PEO and *d*-SDS in D₂O (contrast match conditions for the surfactant). The concentration and molecular weight of PEO are 1.15% w/v and 250 000, respectively. Variations are the following: polymer alone (filled circles); with 100 mM *d*-SDS (filled squares); with 100 mM *d*-SDS and 0.1 M sodium chloride (open triangles); and with 100 mM *d*-SDS and 0.68 M sodium chloride (open circles).

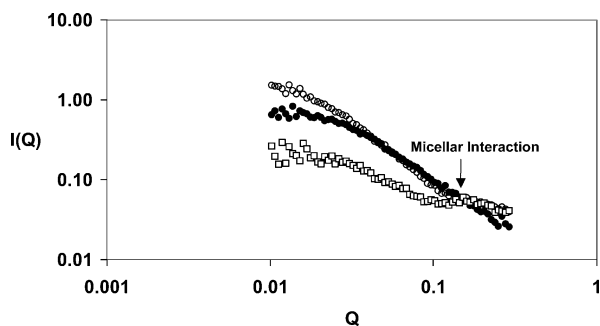


Figure 6. Intensity of neutron scattering as a function of the wave vector (in inverse Å) for mixtures of PEO and *d*-SDS in D₂O. The concentration and molecular weight of PEO are 2% w/v and 107 000, respectively. Variations are the following: polymer alone (filled circles); with 100 mM *d*-SDS and 0.6 M sodium chloride (open circles); and with 400 mM *d*-SDS and 0.6 M sodium chloride (open squares).

corresponds to a minimum in viscosity in Figure 2. Here, one sees primarily the effects of attractive interactions between micelles and polymer coils. As noted by Cabane and Duplessix,²¹ the attraction of micelles to polymer coils results in a weakly coupled system, the behavior of which can be analyzed by linear response theory. The consequences of this are an increase in scattering at low Q and the appearance of a “peak” at high Q due to intermicellar correlations. In other words, features of micellar interaction are observable even under contrast-match conditions for the surfactant, depending on the extent of coupling.²¹ The peak at high Q is clearly seen in the scattering of a lower molecular weight polymer at higher SDS concentration in the presence of salt (Figure 6).²² One might ask why individual micelles are so strongly attracted to polymer coils, particularly at high salt concentrations. As discussed in earlier publications,²³ computer simulations indicate that at any instant the surface of a micelle is made up of both polar headgroups and nonpolar hydrocarbon segments from the relatively fluid micelle core. The adsorption of an amphiphilic polymer on the surface of a micelle reduces the relatively high interfacial energy of the hydrocarbon–water interface.²⁴ Recent work has shown that the reduction in the free energy of micellization of polymer-bound micelles relative to regular or unbound micelles is greater for more hydrophobic polymers.^{6,25} We may therefore expect stronger interaction between PEO and individual SDS micelles at high levels of salt (0.68 M sodium chloride) since the presence of salt makes the PEO coil less

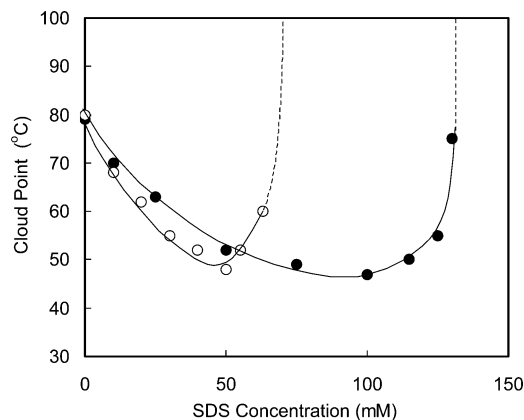


Figure 7. Cloud point of PEO in water ($M_w = 250\,000$) in the presence of 0.68 M sodium chloride as a function of the SDS concentration: 1.15% w/v polymer (open circles) and 2% w/v polymer (filled circles).

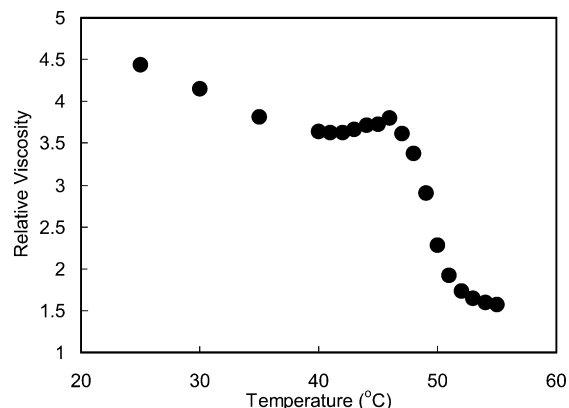


Figure 8. Viscosity of mixture containing 1.15% w/v PEO ($M_w = 250\,000$), 50 mM SDS, and 0.68 M sodium chloride relative to that of 0.68 M sodium chloride as a function of temperature.

hydrophilic as evidenced by a significant decrease in the θ temperature (from 96 °C to 80 °C). The scattering data appears consistent with the viscosity measurements of Figure 2. It is interesting to note that the slope of the curve ($\log I(Q)$ versus $\log Q$) in Figure 5 in the intermediate Q range changes from -1.6 to -2 upon addition of 100 mM surfactant and 0.68 M sodium chloride. Although one has to be careful about interpreting this in terms of a decrease in solvent quality for the polymer in view of the aforementioned coupling of polymer coils to micelles and its influence on scattering, it does, nevertheless, raise an important question. Does the attachment of micelles to the polymer coil at high salt concentrations make the coil less hydrophilic?

Figure 7 shows cloud points of PEO (SE-30) in water containing 0.68 M sodium chloride as a function of the SDS concentration. Focusing, first, on the lower polymer concentration (1.15% w/v), the cloud point decreases significantly from about 80 °C in the absence of SDS to about 48 °C at 50 mM SDS. At concentrations beyond 50 mM, there is a sharp increase in the cloud point. Eventually, upon further addition of SDS, a cloud point cannot be detected in the temperature range below 90 °C.²⁶ A similar pattern is observed on increasing the polymer concentration to 2% w/v. The minimum value of the cloud point is still 48 °C. However, the SDS concentration corresponding to the minimum shifts to about 90 mM, suggesting that the minimum in the cloud point occurs at a fixed ratio of surfactant to polymer. Figure 8 shows viscosity of the polymer–surfactant mixture corresponding to 1.15% w/v PEO, 50 mM SDS, and 0.68 M sodium chloride, relative to that of the aqueous salt

solution (0.68 M sodium chloride) as a function of temperature. The curve exhibits a sharp discontinuity at the boundary between the homogeneous and two-phase regions. The temperature at discontinuity is nearly the same as the cloud point in Figure 7. As expected, there is a significant drop in relative viscosity at temperatures beyond the transition. The small increase in viscosity just below the transition has been observed previously by Wolf and co-workers²⁷ in solutions of polystyrene in cyclohexane and analyzed theoretically by Fixman.²⁸

The results shown in Figures 2–6 are best understood on the basis of the model of Shirahama and co-workers,²⁹ and its refinement by Pincus et al.³⁰ The essential feature of this model is that the attraction of segments of the polymer chain to a spherical micelle is opposed by the entropic cost of deforming a coil to increase the number of contacts on the surface of the micelle and the high excluded volume energies resulting from localization of the adsorbed chain to a finite volume of space. The last two quantities restrict the number of segments associated with a micelle. If the length of the coil is much greater than the size of a micelle and the total number of segments is given by N , only a portion, N^* ($N^* < N$), will be associated with the micelle. The remainder of the coil will continue its random walk trajectory attaching to other micelles. In other words, if there are n micelles, the number of segments involved in the random walk is reduced by nN^* . Because the end-to-end distance is proportional to the number of segments in the random walk raised to the power ν , where ν is the excluded volume exponent,^{19,31} it follows that the coil will continue to shrink as more and more micelles attach to it. This will be the only major conformational change in the concentration range $CAC < c < c_m$ at temperatures close to room temperature. However, for $c > c_m$, the *net* effect is an expansion of the coil because of electrostatic repulsions between attached micelles.

To explain the results of Figures 7 and 8, we consider first the effect of temperature on PEO in water in the absence of surfactant. At room temperature, water is a good solvent for PEO because water molecules attach to the polymer chain by hydrogen bonding.³² However, the attachment necessitates specific orientations of bound water that lead to more unfavorable entropic contributions to the free energy of mixing at higher temperatures. Eventually, this outweighs the favorable enthalpy change of hydrogen bonding, resulting in phase separation. Therefore, what happens when micelles attach to the polymer? In solutions that contain only polymer, it has been suggested that increased monomer–monomer contacts at higher concentrations suppress hydrogen bonding between solvent and polymer.³² Similarly, we might expect the attachment of segments of a polymer coil to micelles to also interfere with hydrogen bonding, resulting in partial dehydration of those segments. If there are two types of segments, A and B, type A segments are attached to micelles, whereas type B segments are not. Interactions between type B segments (B–B interactions) will be the usual excluded volume interactions of PEO segments in a good solvent. Interactions between type A segments (A–A interactions) will be mainly electrostatic because the segments are attached to micelles, but the probability of electrostatic repulsion between micelles will be small at surfactant concentrations below c_m . On the other hand, the likelihood of an interaction between A and B segments will be greater. But in this case, excluded volume repulsions will be *weaker* than B–B interactions because the A segments are partially dehydrated. The weaker interaction will result in collapse of the polymer coil at a lower temperature. In other words, the cloud point will go on decreasing as the number of

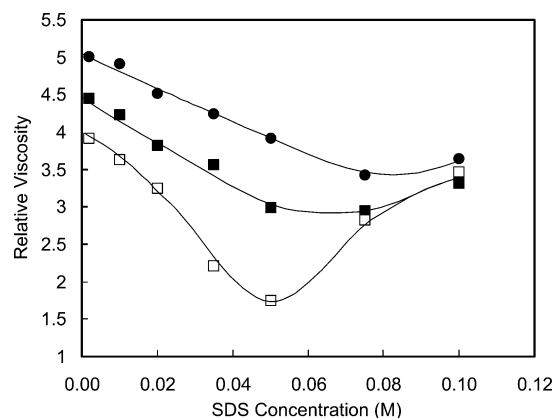


Figure 9. Viscosity of aqueous PEO ($M_w = 250\,000$, 1.15% w/v polymer, and 0.68 M sodium chloride), relative to that of 0.68 M sodium chloride as a function of the SDS concentration at different temperatures: 30 °C (filled circles); 40 °C (filled squares); and 55 °C (open squares).

type A segments increase until the concentration c_m is reached. Beyond this concentration, electrostatic interactions between micelles will prevent collapse of the coil. One might ask why c_m in Figure 2 (corresponding to 0.68 M sodium chloride) is close to 100 mM, but the minimum in the cloud point in Figure 7 for the same polymer concentration occurs at an SDS concentration of 50 mM. Figure 9 indicates that c_m does, indeed, decrease as a function of temperature. The variation of c_m with temperature may be understood as follows. The aggregation number of spherical micelles is given by²³

$$N_{Ag} = 4\pi R_m^3/3V \quad (2)$$

where V is the volume of a surfactant hydrocarbon chain. Since V is a function of the chain length alone, it is a constant for a given surfactant molecule;²³ therefore, we may write $N_{Ag} \sim R_m^3$. Making this substitution in eq 1 and assuming that κ^{-1} is small compared to R_m at high salt concentrations (cf Figure 9), we obtain

$$c_m \sim R_g^3 \quad (3)$$

According to eq 3, the variation of c_m with temperature is simply proportional to the variation of R_g^3 or coil volume with temperature. So what is the relationship between R_g and temperature? The influence of temperature on semidilute solutions of flexible polymers has been investigated in detail.³³ At temperatures sufficiently far from the θ point (in the good solvent regime) R_g follows the scaling relation

$$R_g \sim \tau^{1/8} \quad (4)$$

where $\tau = (\theta - T)/\theta$; T and θ are the absolute temperatures of the polymer solution and the theta point, respectively. Equation 4 may be derived by treating the polymer chain as a series of “thermal blobs”. Inside each blob excluded volume interactions are small compared to the thermal energy $k_B T$, and the behavior of the chain is close to ideal.³⁴ The size of the thermal blob varies with temperature as $\xi_T \approx b\tau^{-1}$, where b is the Kuhn segment length.³⁵ We will assume that eq 4 is applicable in the presence of attached micelles in the noninteracting regime. As stated previously, we take the view that each micelle that attaches to the coil results in weaker excluded volume interactions. This is equivalent to a reduction in the theta point or an

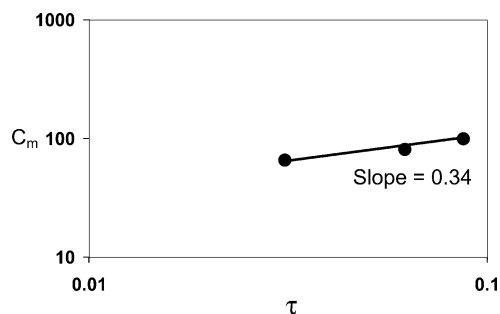


Figure 10. Relationship between c_m (millimoles per liter) and the reduced temperature.

increase in the size of the thermal blob. Combining eqs 3 and 4 we have

$$c_m \sim \tau^{3/8} \quad (5)$$

Equation 5 suggests that a plot of $\log c_m$ versus $\log \tau$ should give a straight line with slope of $3/8$. If we assume from Figure 7 that there are at least that many noninteracting micelles to reduce θ from 80 to 48 °C, we may use the latter as a basis for calculating τ . Figure 10 shows a plot of $\log c_m$ versus $\log \tau$ for temperatures in the range 20 to 40 °C with θ equal to 48 °C. The best-fit experimental slope of 0.34 is just slightly lower than the theoretical estimate. The agreement is fairly good considering the assumptions that went into the derivation of eq 5 and the limited experimental data.

Closing Remarks

In summary, the association of PEO with SDS micelles at room temperature in the regime where electrostatic interactions between micelles is not significant leads to a contraction of the polymer coil in accordance with the theory of Pincus et al.³⁰ The attached but noninteracting micelles also make the coil less hydrophilic and induce phase separation that is observable at higher temperatures. The minimum in viscosity beyond the CAC represents the point at which electrostatic interactions become important. The minimum is more pronounced and shifts to lower surfactant concentrations at temperatures above ambient. We present a tentative model to explain the observed changes in cloud point as a function of surfactant concentration and the shift in viscosity minimum with temperature. We note that, if left undisturbed after heating above the cloud point, a gellike phase containing polymer and surfactant settles to the bottom of a vial containing the sample. The segregation of a gellike phase from a solution containing polymer adsorbed on noninteracting small objects, such as micelles, has been predicted by Alexander.³⁶

Note Added in Proof. After the acceptance of this paper for publication, we came across a paper by Karlstrom et al. (ref 37) that has treated cloud points in polymer-surfactant systems from a different point of view.

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