

Nonionic Surfactant and Temperature Effects on the Viscosity of Hydrophobically Modified Hydroxyethyl Cellulose Solutions

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Nonionic surfactant and temperature effects on the viscosity of hydrophobically modified hydroxyethyl cellulose (HMHEC) solutions are investigated experimentally. Weak shear thickening at intermediate shear rates takes place for HMHEC at moderate concentrations and becomes more significant at lower temperatures. While this amphiphilic polymer in surfactant-free solution does not turn turbid by heating to 95 °C, its mixture with nonionic surfactant shows a lower cloud point temperature than does a pure surfactant solution. For some mixture cases, phase separation takes place at temperatures as low as 2 °C. The drop of cloud point temperature is attributed to an additional attractive interaction between mixed micelles via chain bridging. With increasing temperature, the viscosity of an HMHEC–surfactant mixture in aqueous solution first decreases but then rises considerably until around the cloud point. The observed viscosity increase can be explained by the interchain association because of micellar aggregation.

1. Introduction

Water-soluble polymers are superior to solvent-borne counterparts for safety and environmental concern and have attracted growing attention in industry. They are widely used to modify the rheological properties of various water-based formulations, such as latex paints, drilling mud, and cosmetics. In many cases, the polymer is modified by adding alkyl side chains either randomly along the backbone or to its two ends as hydrophobes, to become amphiphilic. Such a modification can lead to interactions of more kinds with other species in a solution, and thereby more versatile flow behavior, depending on the solution composition. In this paper, we will study the effects of nonionic surfactant and temperature on the viscosity and microstructure of a hydrophobically modified polymer (HMP) in aqueous solution.

A main feature of HMP is association between hydrophobes, which can be either interchain or intrachain. At sufficiently high polymer concentration, a dramatically high viscosity can be attained because of the formation of a gel-like structure arising from the dominant intermolecular association.¹ The hydrophobe association may be enhanced or weakened by an imposed flow, depending on the flow strength and polymer concentration.² The association is also affected by the presence of surfactant via interactions of various kinds. One of the most important interactions is hydrophobic binding between the HMP hydrophobes and the surfactant tails to form so-called “mixed micelles”.³ At low surfactant concentration, this binding enhances the interchain association for gel-like HMP solutions, leading to an increase in viscosity.^{4–7} Further addition of the

surfactant can result in an increased number of mixed micelles, each of which, however, contains hydrophobes in a declined number. As a result, the viscosity will reach a maximum and then decrease. With excess surfactant, each hydrophobe will eventually be masked by a mixed micelle, leading to disappearance of the hydrophobe links and formation of free micelles. This behavior is reflected by a nearly constant viscosity since the HMP has been saturated with surfactant and the free micelles exert a very small effect on the viscosity. For ionic surfactant, the electrostatic repulsion between the mixed micelles can affect the polymer conformation and the corresponding gel microstructure.^{5–7}

For nonionic surfactant, the mechanism of dissolution in water is hydrogen bonding between its hydrophilic head (usually an ethylene oxide chain) and water molecules. An increase in thermal energy (i.e., temperature rise) can weaken the bonding, causing the solution to turn turbid at a certain temperature because of dehydration of the ethylene oxide (EO) units and consequent micellar aggregation. This temperature is called cloud point temperature (CPT),⁸ which in principle depends on the length of the EO chain and the size and structure of the hydrophobic tail. The cloud point temperature has been found to increase with increasing number of EO units, decreasing hydrocarbon tail and increasing degree of branching.⁸ Also, the surfactant concentration can affect the cloud point. Right above the cloud point, the solutions will separate into a surfactant-lean and a surfactant-rich phase; the latter involves micellar aggregation.

Addition of polymer to a surfactant solution can change the clouding behavior of the surfactant. The CPT of oligoethylene glycol ether (C_xE_y) was depressed by the presence of water-soluble polymers, such as ethylhydroxyethyl cellulose,⁹ poly-

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(ethylene glycol),^{10,11} and agarose coils.¹² The observed depression was explained by depletion flocculation because the interaction between the polymer and surfactant is primarily volume exclusion, leading to a segregative phase separation¹³ into a polymer-rich and a surfactant-rich solution. In the absence of surfactant, the former two polymers in aqueous solutions can also turn turbid by heating, whereas the latter undergoes a gel–sol transition.

For hydrophobically end-capped poly(ethylene oxide) (an uncharged telechelic HMP), Alami et al.¹⁴ investigated the effect of addition of C_xE_y on the CPT of HMP. In their experiments, the HMP solution showed a clouding behavior, even in the absence of surfactant, owing to a phase separation into a dilute and a concentrated polymer solution. The latter contains an extended transient polymer network with hydrophobic nodes. In addition, they found that the presence of nonionic surfactant can decrease the CPT of the HMP and ascribed this behavior to the stabilization of the network and nodes. Appell et al.¹⁵ also observed such a declination and attributed it to an additional intermicellar attraction because of chain bridging inferred from small-angle neutron scattering. The phase behavior of a mixture of charged HMP and nonionic surfactant and the corresponding rheology have also been investigated.^{16–18} It was reported that the solution may undergo thermal gelation by heating and become very viscous, thanks to a transition to large vesicles bridged by the polymer chains. The temperature effect on the flow dynamics of a charged HMP–surfactant mixture was examined by Tirtaatmadja et al.¹⁹ While the viscosity showed an Arrhenius behavior in their work, our recent study on mixtures of hydrophobically modified hydroxyethyl cellulose (HMHEC) and Tergitol 15-S-7 found that the viscosity may slightly increase with temperature.²⁰

The influence of uncharged HMP with randomly distributed hydrophobes on the clouding phenomenon of surfactant has not yet been investigated but is expected to be more complicated since the hydrophobic interactions are not restricted to the polymer chain ends. In this study, we will examine the effects of nonionic surfactant and temperature on the phase and viscosity behaviors of HMHEC in an attempt to seek the correlation between molecular interactions and flow behavior. In addition to the random distribution of hydrophobes, we would like to point out another important difference from the prior studies.^{14,15} The polymer solution in our work does not turn cloudy in the absence of nonionic surfactant for temperature up to about 95 °C.

2. Experimental Section

2-Hydroxyethyl cellulose hydrophobically modified with hexadecyl groups (HMHEC) from Aldrich was used as supplied in this study. According to the manufacturer, the polymer has a molecular weight $M_w = 560\,000$ g/mol with the molar and degree substitutions being 2.7–3.4 and 2.0, respectively. The surfactants used are nonionic, including $C_{12}E_5$ (pentaethylene glycol monododecyl ether) and $C_{12}E_6$ (hexaethylene glycol monododecyl ether). According to the manufacturer, they are highly monodisperse. Thus, the effect due to the polydispersity of the surfactant hydrophilic moiety is eliminated. They were used without further purification. The specifications of the two surfactants are given in Table 1.

Stock solutions of 1.2 wt % HMHEC were prepared by dissolving the dry powder in deionized water that had been further purified through a Millipore MilliQ purification system and had resistivity of 18.0 M Ω cm. The solutions were magnetically stirred for 2 h at 40 °C, and they were then cooled

TABLE 1: Specifications of Nonionic Surfactants

surfactant	molecular formula	M_w^a g/mol	CMC ^a ppm	manufacturer
$C_{12}E_5$	$CH_3(CH_2)_{11}(OCH_2CH_2)_5OH$	406.5	27.6	Fluka
$C_{12}E_6$	$CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$	450.6	30	Sigma

^a Provided by supplier.

to the room temperature before mixing with a proper amount of the surfactant stock solutions to achieve the desired final composition. The mixtures were then stirred again till a homogeneous solution was obtained. Samples were stored in a refrigerator for at least 24 h to complete hydration and interactions. All the samples were used for measurement within 1 week to avoid contaminations and degradations.

The cloud point experiments were carried out in a water bath (Polyscience) equipped with a digital temperature controlled unit within 0.1 °C. The temperature changing rate of the water bath is 1 °C/min. Each sample of approximately 10 mL placed in a screw-capped glass tube was heated in the water bath. The cloud point was determined by visual observation of the onset of an obvious turbidity change. Heating and cooling were regulated around the cloud point. The reproducibility of the CPT measurement was good within 0.5 °C, and the average value was taken from triplicate measurements. The solution viscosity was measured using a Haake RS75 rheometer with a DC50 temperature controller (water circulating bath). A double concentric-cylinder (DG41) geometry or a cone-and-plate (C60/4, cone diameter and angle are 60 mm and 4 °) fixture was used to carry out the measurements, depending on the solution viscosity and shear rate range.

3. Results and Discussion

3.1 Temperature Effect on Pure HMHEC Solutions. We first examine the behavior of surfactant-free HMHEC solutions. Using the same HMHEC as in this study, Maestro et al.¹ measured the interfacial tension of polymer water solutions and toluene to deduce a very low critical aggregation concentration (CAC) of about 0.0004 g/dL. They also measured the reduced viscosity of HMHEC at various concentrations and found that the reduced viscosity exhibited a sharp increase at about 0.15 g/dL, which is comparable to the value reported for shorter HMHEC ($M_w = 300\,000$ g/mol) by Nishikawa et al.²¹ For dilute solutions (<0.15 g/dL), Nishikawa et al. also carried out fluorescence probe experiments to conclude that the aggregation number of HMHEC micelles should be about 10 or less. It can thus be inferred that when the HMHEC concentration is between 0.0004 g/dL and 0.15 g/dL, small aggregates, each of which consists of a few chains, are formed because of hydrophobe linking, somewhat similar to the flower micelles of a telechelic HMP. At 0.15 g/dL, the aggregates start to associate to form a gel (network), analogous to the loop-to-bridge transition of a telechelic HMP.

Figure 1 plots the viscosity of 0.4 wt % HMHEC solutions against shear rate at various temperatures. This concentration is higher than 0.15 g/dL, implying a certain extent of gelation in the absence of flow. Typically, the viscosity at a given shear rate decreases with increasing temperature. It can also be seen that weak shear thickening takes place at moderate shear rates, followed by shear thinning. A similar behavior was also observed for 0.35 wt % and 0.5 wt % solutions from our experiments, although the results are not shown here. The intriguing shear thickening phenomenon of HMHEC at intermediate shear rates, which was previously noticed by Maestro et al. for 0.5 wt % solution,² is attributed to the shear enhanced

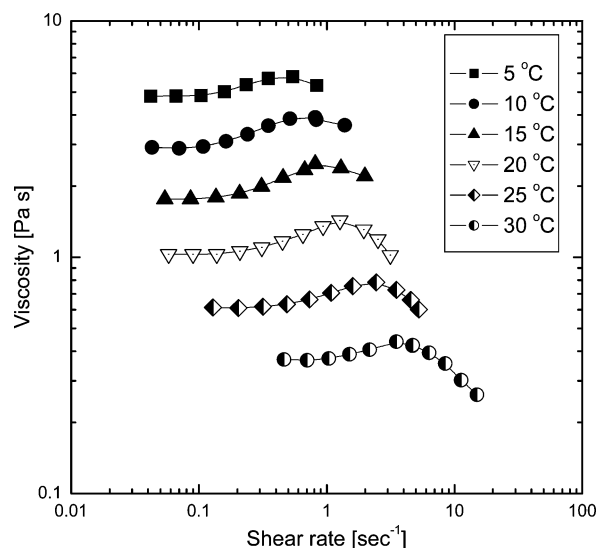


Figure 1. Steady-state flow curve of pure 0.4 wt % HMHEC at various temperatures.

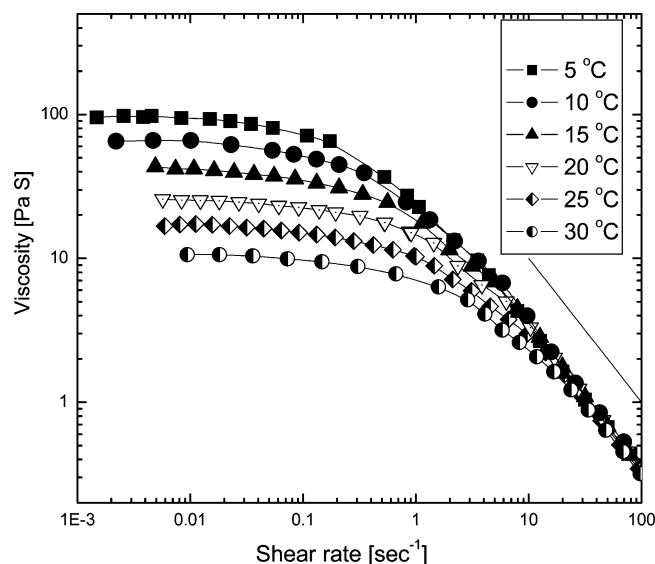


Figure 2. Steady-state flow curve of pure 1 wt % HMHEC at various temperatures.

interchain association of hydrophobes as the imposed flow elongates and aligns the polymers to promote the intermolecular bridging via the hydrophobic interaction. In a stronger flow, however, the links can be disrupted, and thus the solution becomes shear thinned. It can be found from Figure 1 that the thickening behavior shifts to lower shear rates at lower temperatures. Since hydrophobes possess a lower thermal energy at a lower temperature, a weaker flow suffices to promote interchain association and also the hydrophobes involved are more unlikely to escape the resulting associate.

Figure 2 plots the flow curves of 1 wt % HMHEC at various temperatures. In contrast to the behavior of 0.4 wt % solutions, no shear thickening is observed in the shear rate range investigated. The different behavior can be understood because at high enough concentrations, HMHEC molecules already entangle substantially, leading to a considerable degree of interchain association as reflected by a much higher viscosity than that of 0.4 wt %. Therefore, the molecular elongation caused by an imposed external flow can hardly give rise to noticeable enhancement in the chain bridging for the formation of a stronger network. Instead, the flow at high enough shear

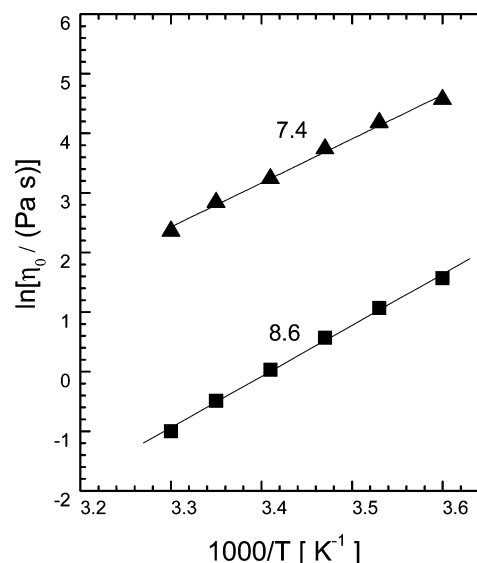


Figure 3. Arrhenius plots of zero-shear viscosity of pure 0.4 wt % (square) and 1 wt % (triangle) HMHEC solutions. The slopes of the fitting lines are shown as well.

rate simply disrupts the existing hydrophobe associates and results in the significant shear thinning. The slopes of the curves in Figure 2 are all around 1 at high enough shear rates, typical of a gel behavior that the viscosity dramatically drops associated with the gel–sol transition at a critical stress.²²

The logarithm of zero-shear viscosity is plotted against the reciprocal temperature in Figure 3. The good linear fit seen in the figure indicates that the zero-shear viscosity of the HMHEC solution exhibits an Arrhenius behavior. The activation energies of dissociation determined from the fitting lines are 62.1 and 71.2 kJ/mol for 1% and 0.4% solutions, respectively, comparable to the estimate of 60 kJ/mol by Maestro et al. from the relaxation time.¹ For the HMHEC solutions, we also conducted cloud point experiments from 20 °C to 95 °C but did not observe any clouding phenomenon.

3.2 Clouding Behavior of HMHEC–Surfactant Solutions.

For pure surfactant solutions, the turbidity at cloud point arises from the formation of a surfactant-rich phase because of the micellar flocculation. It is associated with the breakup of hydrogen bonds between the hydrophilic heads and water molecules. As mentioned in the Introduction, CPT depends on the sizes of hydrophilic and hydrophobic moieties. In this regard, our observation indicates that up to 95 °C, the increased thermal energy is not sufficient to break hydrogen bonds between the HMHEC backbone and water molecules so as to make clouding or phase separation occur. The explanation to this behavior is twofold. First, the alkyl hydrophobes are not sufficient both in length and quantity. Second, the existence of the hydroxyl groups of HMHEC gives rise to stronger hydrogen bonding with water.

We now investigate the effect of HMHEC on the CPT of nonionic surfactants, C₁₂E₅ and C₁₂E₆, that possess the same hydrophobic moiety. Figure 4 shows the variation of CPT with HMHEC concentration for 1 wt % surfactant solutions. When the HMHEC concentration exceeds 1 wt %, the solution becomes quite viscous and difficult to be handled. Also, the solution appears slightly turbid, which may affect the accuracy in the CPT determination for the mixture cases. Therefore, in this study, the maximum concentration of HMHEC is limited to 1 wt %. Figures 5 and 6 present the variation of CPT with the surfactant concentration for cases without and with the presence of HMHEC at 0.4 wt %. 2 °C is the lowest temperature

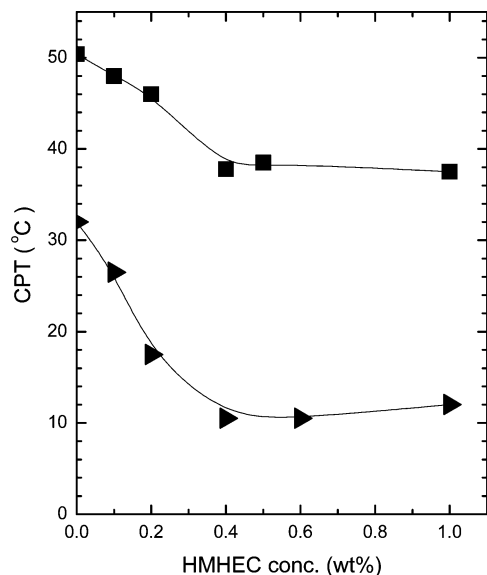


Figure 4. Cloud point temperature of 1 wt % surfactant solutions with addition of HMHEC; C₁₂E₅ (triangles), C₁₂E₆ (squares).

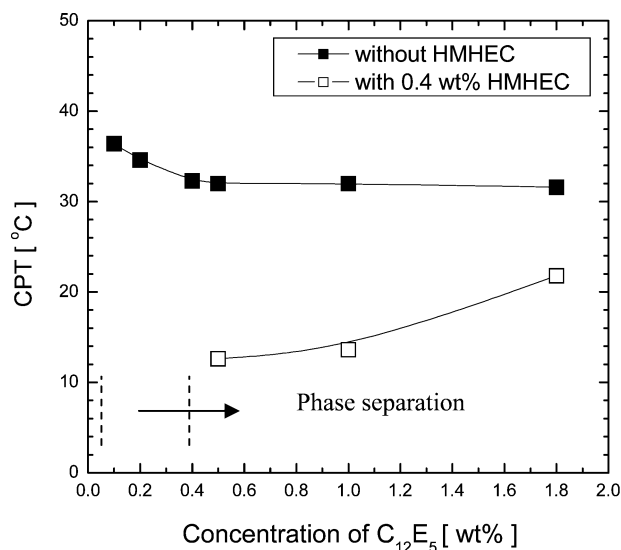


Figure 5. Cloud point temperature as a function of C₁₂E₅ concentration without HMHEC and with 0.4 wt % HMHEC. For the latter, macroscopic phase separation occurred even at 2 °C (lowest temperature investigated) in the region between the dashed lines.

investigated in the present study. It can be found from Figures 4–6 that the presence of HMHEC lowers CPT as compared to that for the corresponding pure surfactant solution. In the presence of 0.4 wt % HMHEC, the solutions at low enough surfactant concentrations have already phase-separated even at a temperature as low as 2 °C, and thus no corresponding CPT data are seen in Figures 5 and 6. After separation into two macroscopic phases, the viscosity of the dense phase that appears white is very viscous, while the light phase is clear and has a viscosity about twice the value of water.

3.3 Viscosity Behavior of HMHEC–Surfactant Solutions.

To understand the clouding behavior of the mixture, we must examine the interactions between HMHEC and surfactant. It has been well-known that surfactant molecules may bind onto the hydrophobes of the polymers to form mixed micelles. Each mixed micelle may contain several hydrophobes either from a chain or from different chains. At sufficiently low concentrations, there exist no free micelles since nearly all surfactant molecules are associated with the polymer, enhancing the

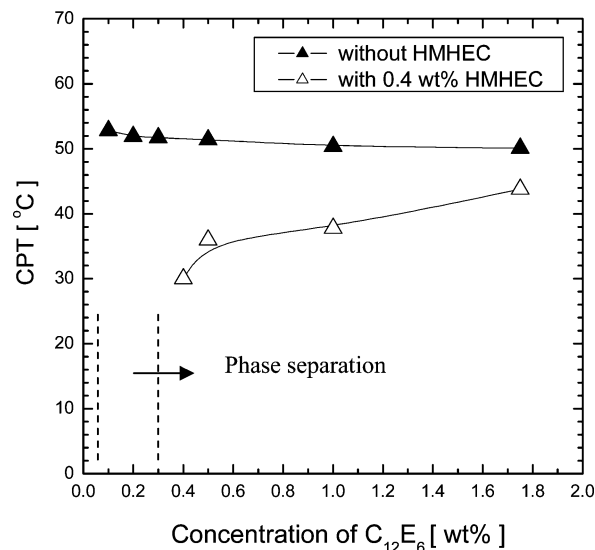


Figure 6. Cloud point temperature as a function of C₁₂E₆ concentration without HMHEC and with 0.4 wt % HMHEC. For the latter, macroscopic phase separation occurred even at 2 °C (lowest temperature investigated) in the region between the dashed lines.

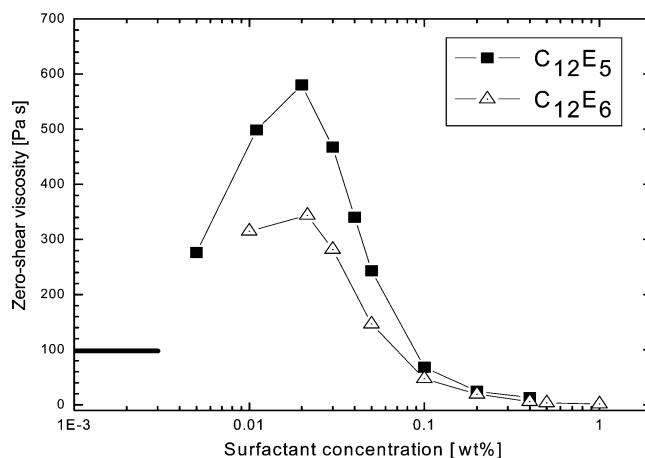


Figure 7. Zero-shear viscosity of 1.0 wt % HMHEC with addition of nonionic surfactant as a function of surfactant concentration at 5 °C. The short horizontal line indicates the value in the absence of surfactant.

hydrophobe association. The enhancement strengthens the network when the HMHEC concentration exceeds the critical value for gelation. This is evidenced by the increase of zero-shear viscosity with the increasing surfactant concentration as shown in Figures 7 and 8 for 1 wt % and 0.4 wt % HMHEC, respectively. Beyond the viscosity maximum, a progressive increase in surfactant concentration reduces the average number of hydrophobes in each mixed micelle, which eventually becomes a small single-digit value. At this concentration, the hydrophobes are masked by excess surfactant, and the binding between surfactant and polymer is deemed saturated. Hence, a further increase in surfactant concentration can give rise to the formation of free micelles. This behavior is indeed reflected by the viscosity decrease toward a constant as seen in Figures 7 and 8. Phase separation takes place in 0.4 wt % HMHEC solutions with surfactant concentration ranging from 0.1 to 0.3 wt %, and hence no viscosity data are available. The asymptotic viscosity at high surfactant concentrations is even lower than the value of HMHEC alone. When the surfactant concentration exceeds the saturation value, the intermolecular association is disrupted substantially, thereby leading to an increased ease of deforming the material. The saturation concentration can be

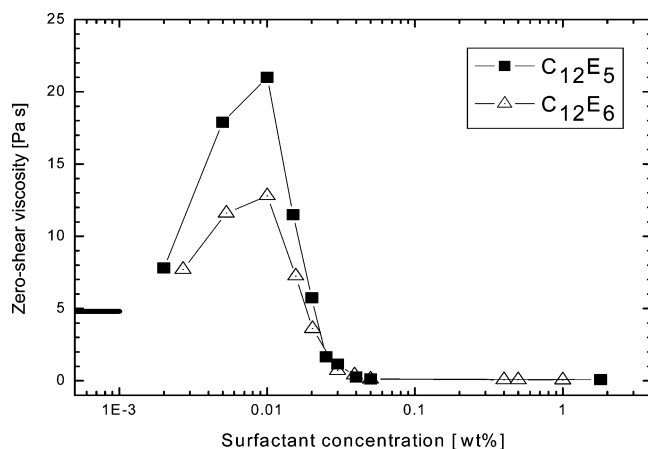


Figure 8. Zero-shear viscosity of 0.4 wt % HMHEC with addition of nonionic surfactant as a function of surfactant concentration at 5 °C. The short horizontal line indicates the value in the absence of the surfactant.

crudely estimated by the concentration at which the viscosity becomes nearly a constant. From Figures 7 and 8, the surfactant concentrations for saturation are about 0.2 wt % and 0.04 wt % for 1 wt % and 0.4 wt % HMHEC, respectively. These results indicate that the CPT results shown in Figures 4–6 are all under the condition that the hydrophobes have been masked by the surfactant.

For $C_{12}E_6$ solutions with addition of hydrophobically end-capped PEO in a small amount, Appell et al. observed a reduction of cloud point temperature.¹⁵ Below but near the cloud point, they detected an attractive force between micelles from small-angle neutron scattering and attributed this force to some polymer molecules, each of which links two mixed micelles. A similar bridging behavior can be expected for HMHEC as each chain contains more than two hydrophobes. With sufficient addition of surfactant, there exist both free and mixed micelles. Since the mixed micelles on a same polymer are indeed linked together, their aggregation at elevated temperatures because of weakened hydrogen bonding is enhanced.¹⁵ As a result, the solution can turn cloudy at a lower temperature than in the absence of HMHEC. It can be seen from Figures 5 and 6 that the declination of cloud point temperature is less substantial for higher surfactant concentrations. This behavior can be explained by the comparatively large amount of free micelles, on which the polymer chains exert no direct effect, as opposed to coexisting mixed micelles. As can be seen in Figure 4, at a fixed surfactant concentration, a smaller drop in CPT occurs for lower HMHEC concentrations. When the mixed micelles greatly outnumber the free micelles, the linking effect of HMHEC can indeed result in phase separation at very low temperatures, as shown in Figures 5 and 6. A dramatic reduction of CPT was also reported by Appell et al. for mixtures of $C_{12}E_6$ and end-capped PEO.¹⁵

We now examine the temperature effect on the viscosity of HMHEC solutions with added surfactant. Figure 9 plots the viscosity for the cases with $C_{12}E_5$, while Figures 10 and 11 present the results for $C_{12}E_6$. The CPTs for various cases are indicated in the figures. It can be found that the temperature dependence of the solution viscosity no longer follows the Arrhenius behavior, as opposed to pure HMHEC solutions. For the case of $C_{12}E_6$, Figure 10 shows that the mixture viscosity first decreases, reaches a local minimum, and then increases till around the cloud point temperature. The viscosity can rise by a factor of 2 with respect to the local minimum. For $C_{12}E_5$, on the contrary, the viscosity increases right from the lowest

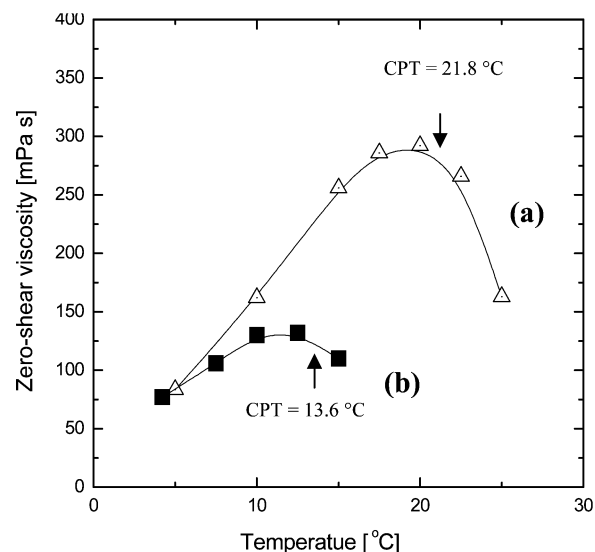


Figure 9. Temperature dependence of zero-shear viscosity for (a) 0.4 wt % HMHEC + 1.8 wt % $C_{12}E_5$ and (b) 0.4 wt % HMHEC + 1.0 wt % $C_{12}E_5$.

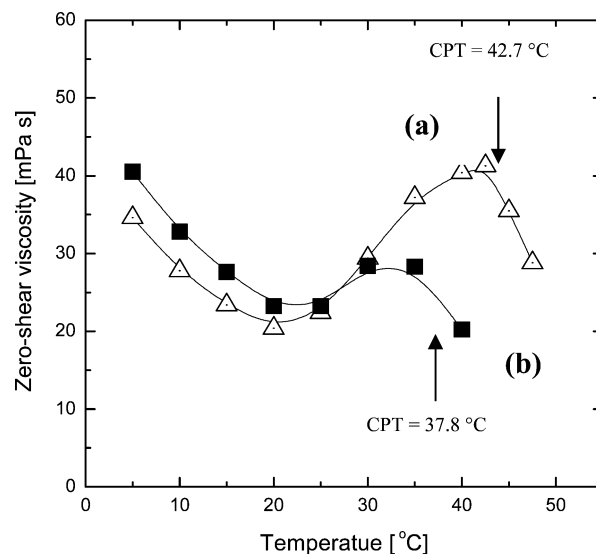


Figure 10. Temperature dependence of zero-shear viscosity for (a) 0.4 wt % HMHEC + 1.8 wt % $C_{12}E_6$ and (b) 0.4 wt % HMHEC + 1.0 wt % $C_{12}E_6$.

temperatures investigated till about the cloud point. The viscosity increase can be even 3-fold as shown in Figure 9. The viscosity increase is more significant than for HMHEC + Tergitol 15-S-7 in our previous study.²⁰ The viscosity data beyond the cloud point shown in these figures are the values measured 5 min after each temperature is reached. For these cases, the solution stability will be discussed in detail later.

The interesting temperature dependence below the cloud point can be explained by a competition between Arrhenius behavior and micellar aggregation. At low enough temperatures, hydrogen bonding between the hydrophilic moiety of $C_{12}E_6$ and water is strong. Therefore, aggregation between micelles is unlikely and the viscosity simply shows an Arrhenius behavior. At higher temperatures, the thermal energy weakens the hydrogen bonds considerably, thereby leading to micellar aggregation. Some aggregation involves mixed micelles on different chains and can directly give rise to interchain association. Even the aggregation between mixed micelles on a same chain can bring polymer molecules closer because the involved mixed micelles may have already been linked with other chains. Both account

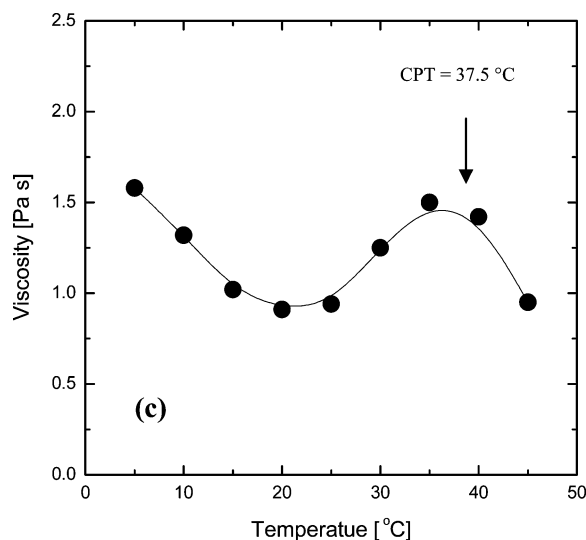


Figure 11. Temperature dependence of viscosity at 0.2 s^{-1} for 1.0 wt % HMHEC + 1.0 wt % C_{12}E_6 .

for the viscosity rise till the cloud point. Since the number of EO units in the hydrophilic head is lower for C_{12}E_5 than for C_{12}E_6 , the micellar aggregation can take place at lower temperatures for C_{12}E_5 , and this explains why the viscosity increase is seen at comparatively low temperatures. In our prior investigation on 1 wt % HMHEC + 2 wt % Tergitol 15-S-7,²⁰ the measured radius of gyration from static light scattering was found to increase with temperature from 20 °C to 35 °C (about CPT), while the corresponding pure HMHEC solution showed an opposite trend. This similar temperature dependence for the size and viscosity of HMHEC–surfactant complexes provides an additional support to the above argument for aggregation, which can indeed take place before the solution becomes visibly cloudy. For further verification, one may apply fluorescence probe technique to measure the aggregation number of the micelles.

When the cloud point is reached, the HMHEC–surfactant solution becomes turbid, and a second phase starts to form as droplets. To observe the phase evolution, in this study, the cloudy solutions were placed in the water bath at a temperature slightly higher than the cloud point temperature to stand for some time. We find that for 0.4 wt % HMHEC, the phase separation took hours to days to be complete, resulting in two macroscopic phases: a supernatant above a white viscous phase. The viscosity of the supernatant is only about 2 times as high as water viscosity, indicating that most of the polymer and surfactant form complexes and stay in the white phase. For 1 wt % HMHEC, however, the solution remained cloudy and we could not obtain two macroscopic phases even after 2 weeks. This slow process is attributable to the high solution viscosity as droplets must diffuse to encounter each other and get coalesced so as to gradually become a continuous phase. Since the solution becomes biphasic above the CPT and the phase separation is ongoing, the solution viscosity is essentially time-dependent. To illustrate such a behavior beyond the cloud point, we plot the solution viscosity as a function of time for 0.4 wt % HMHEC + 1.8 wt % C_{12}E_6 in Figure 12. At each temperature, the viscosity was measured as a function of time for a period of 1 min and the second measurement was conducted 3 min later. It can be clearly seen that at 42.5 °C (slightly below CPT), the viscosity is independent of time. At 47.5 °C, in contrast, the solution becomes unstable showing a fluctuating viscosity, and the viscosity even differs in the two

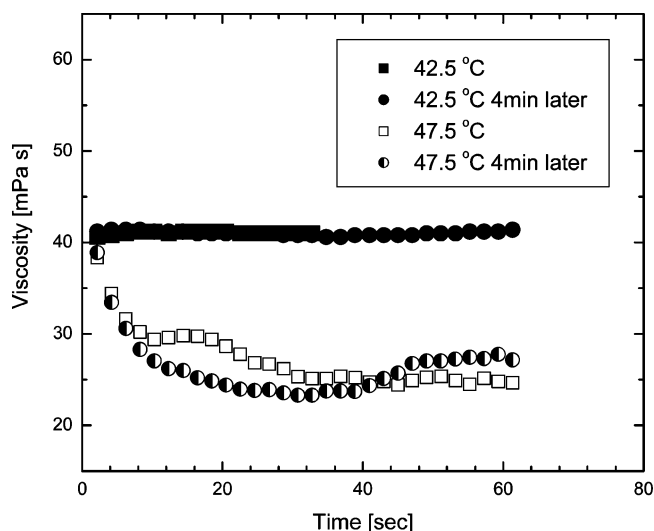


Figure 12. Viscosity of 0.4 wt % HMHEC + 1.8 wt % C_{12}E_6 as a function of time at 2 s^{-1} (low enough for the Newtonian plateau) with temperature fixed at 42.5 °C (slightly below the CPT) and 47.5 °C (4.8 °C above the CPT). Note that at each temperature, the second measurement was conducted 4 min after the starting time of the first.

measurements. It is clearly indicative of a time dependence of viscosity. In this regard, the viscosity trend above CPT shown in Figures 9–11 should be taken with caution, in particular for 0.4 wt % HMHEC since the phase separation is comparatively fast.

3.4 Comparison with the System of Charged HMP. It is interesting to compare the behavior of our system with that involving charged HMP and C_xE_y in the prior works.^{16–18} It has been reported that by heating, a C_xE_y solution with small enough y undergoes a consecutive phase transition in such an order: a single micellar phase, a micellar biphasic, and a lamellar phase which may coexist with a water phase. In the presence of charged HMP, the electrostatic repulsion between polymer segments suppresses the aggregation of mixed micelles and thus stabilizes a single micellar phase. As a result, the micellar biphasic has a shrinking temperature range or even disappears in the phase diagram when the concentration of charged HMP is sufficiently high.^{16,17} For the latter case, the authors observed a local viscosity maximum at a certain temperature and attributed it to reversible thermal gelation associated with the transition from a micellar phase to a lamellar phase. In the lamellar phase, the surfactant forms large vesicles bridged by the polymer chains because of the dissolved hydrophobes in the vesicle bilayer. The corresponding viscosity for some cases could become 10 times as large as the value for the single micellar phase. In our study, where there is no electrostatic repulsion for HMHEC, the solution viscosity increases with temperature prior and near to the cloud point and appears to have a local maximum around the cloud point. Unlike the formation of a monophasic solution of bridged lamella, the phase separation in our system inhibits a further increase in viscosity with temperature. In the work of Iliopoulos and Olsson,¹⁶ the effect of added salt that screened out the electrostatic repulsion between charged HMP was also investigated. They found that with sufficient salt addition, a biphasic solution could exist over a considerable temperature range and the temperature for the transition to the biphasic was lowered as compared to the case of pure surfactant. This finding indeed agrees with our observation using the neutral polymer HMHEC. However, a further comparison cannot be made since no viscosity result was reported by them for the case of added salt.

4. Conclusion

We have conducted an experimental study on the influences of surfactant and temperature in the phase and viscosity behaviors of HMHEC that contains randomly distributed hydrophobes. For surfactant-free HMHEC solutions at moderate concentrations, shear-enhanced hydrophobic association can take place at intermediate shear rates, in particular for low temperatures. For HMHEC–surfactant mixtures, the cloud point temperature is decreased by the presence of the polymer owing to an additional attractive interaction between mixed micelles arising from chain bridging. The variation of viscosity at sufficiently high temperature shows an interesting correlation with the enhanced interchain association caused by the aggregation of mixed micelles prior to the cloud point.

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