

# Interaction between a Nonionic Surfactant and a Hydrophobically Modified 2-Hydroxyethyl Cellulose

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Interaction between the nonionic surfactant Tergitol 15-S-7 and hydrophobically modified 2-hydroxyethyl cellulose (HMHEC) was studied rheologically in a semidilute regime of HMHEC. The low-shear viscosity of HMHEC was increased with addition of surfactant from 25 to 250 ppm, in which the critical micelle concentration of surfactant was near 39 ppm, and then decreased to a value smaller than that of pure HMHEC with further addition of surfactant to 1000 ppm. An interesting shear-induced phenomenon was observed. The steady-state shear measurements show that there exist crossovers between viscosity–shear rate curves of HMHEC solutions with and without surfactant added, whereas it was not observed in the HEC–surfactant systems. Moreover, added Tergitol 15-S-7 reversed the temperature effect on the viscosity of the HMHEC solution. That is, increasing temperature to or near the cloud point raises the viscosity of the HMHEC–surfactant aggregates, in contrast to the viscosity decrease in the pure HMHEC solutions. A possible mechanism based on the necklace model and the clouding phenomenon is conjecturally introduced to explain such phenomena.

## 1. Introduction

Complex aqueous systems containing surfactants and polymers have been the focus of intense fundamental and applied research,<sup>1–4</sup> as they are often formulated conjointly in a wide range of applications. Moreover, during the past decades, introduction of hydrophobically modified (HM) water-soluble polymers to such complex systems has initiated considerable study because of the unusual rheological characteristics exhibited in such systems,<sup>1,3,5–20</sup> making them candidates for viscosity modifiers in many industrial applications, such as water-borne paints, cosmetics, personal-care products, foods, pharmaceuticals, and many others of significant commercial importance.<sup>1</sup>

The HM polymers are those containing small portion of hydrophobic groups or hydrophobes grafted along the hydrophilic polymer backbones<sup>21,22</sup> or attached as the end groups.<sup>16,17</sup> Alone they can form temporary hydrophobic association networks, by either interchains or intrachains, in aqueous media even at relatively low polymer concentrations.<sup>1,22</sup> Addition of surfactant to the HM polymer solutions will affect the association behaviors via interactions of various kinds. In semidilute HM polymer solutions in the presence of surfactant at moderate concentration, viz., near the critical micelle concentration (cmc) of the surfactant, the intermolecular hydrophobic associations are commonly enhanced to give rise to the formation of a gel-like network and mixed micelles, which, in turn, render one or more orders of magnitude in viscosity higher than that of pristine HM polymer solutions.<sup>1,3,5–20</sup> With more surfactant added, the network may be broken and the interactions diminish, as hydrophobes are solubilized or masked by excess surfactant

micelles.<sup>1,5–7</sup> Consequently, the solution viscosity becomes constant and even lower than that of pure HM polymer at the same polymer concentration, since the HM polymers are saturated with surfactants and the free surfactant micelles can have only a little effect on the viscosity.

Usually, interactions between nonionic surfactants and neutral polymers are very weak or even nonexistent because no dominating electrostatic associations, either attractive or repulsive, could be found in such systems.<sup>1,23,24</sup> For example, no sign of interaction was shown between ethoxylated nonionic surfactants and hydrophilic neutral polymers, such as poly(vinyl alcohol), poly(ethylene oxide), poly(vinylpyrrolidone), and various cellulose analogues.<sup>1,9,12,14,24</sup> Indeed, in such neutral complex systems, the interactions between surfactants and polymers result mostly from the hydrophobic interactions between surfactant tails and the hydrophobic moieties of neutral polymers, and some from hydrogen bonding between surfactant headgroups and hydrophilic portions of polymers.<sup>1,25</sup>

Hydrophobic modification of polymers could provide extra hydrophobic attraction between the hydrophobic tails of surfactants and the hydrophobes on the HM polymers. Therefore, the phase behavior of surfactant–polymer system is altered and the level of interaction is increased, leading to a substantial influence on the rheology of the system. In general, polymer–surfactant interaction is found to increase with increasing hydrophobicity of either surfactant or HM polymers.<sup>1,15,27</sup> It is noted that such hydrophobic attractions in the systems having surfactants and HM polymers of the same charge may still be strong enough to overcome the electrostatic repulsion.<sup>6,7,28</sup>

Probably owing to their relatively weak interactions that require extremely sensitive tools for detection, such as NMR, EPR, SANS or SAXS, microcalorimetry, and fluorescence technique,<sup>1,4,23,29,30</sup> until now not many reports available in the open literature have been dedicated to such systems having

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nonionic surfactants and neutral HM polymers.<sup>9,11,12,14,16,31,32</sup> Despite that, surfactant concentrations used in these reports have to be as low as around a few times the cmc or even less, falling in the range where surfactant–polymer interaction is seemingly obvious, to yield experimentally observable interactions.

Some aqueous micellar solutions of nonionic surfactants or polymers exhibit a lower critical solution temperature (LCST), normally referred as the cloud point (CP), at which the micellar solution phase separates into two phases, one rich and the other lean in surfactant or polymer. When micellar solution heated from below the cloud point, micelles aggregate into much larger ones to minimize the free energy of the system owing to the loss of their hydrophilicity. In other words, the hydrophobic effect is enhanced.<sup>33,34</sup> Hence, with proper choices of nonionic surfactants and neutral HM polymers, significant hydrophobic interactions can still be garnered under suitable experimental conditions.

In this study, we have chosen the nonionic surfactant Tergitol 15-S-7 and hydrophobically modified hydroxyethyl cellulose (HMHEC) for studying their interaction by using rheological method and static light scattering technique, in an attempt to provide insight into the nature of hydrophobic interactions. The HMHEC concentration used in this study was ensured to be above its overlap concentration.<sup>10,33</sup> For comparison, its unmodified analogue, hydroxyethyl cellulose (HEC), was adopted as well. We must point out that the cloud point of the 0.5 wt % HMHEC solution used in this work is not found in the range from 25 to 80 °C. The nonionic surfactant Tergitol 15-S-7 was especially chosen because of its low cloud-point temperature near 37 °C,<sup>35</sup> which gives us the experimental convenience to study the effect of temperature on the surfactant–polymer interaction. In part of this work, surfactant concentrations are maintained as high as 2 wt %, near 500 cmc's, so that typical intermolecular hydrophobic association between HM polymers would be prevented by surfactant micelles in excess. As a result, the surfactant–HMHEC solution gives a near zero shear rate viscosity lower than that of a neat HMHEC solution.

Meanwhile, HMHEC shows a normal temperature tendency, namely, viscosity decreasing with increasing temperature. However, addition of 2 wt % Tergitol 15-S-7 surfactant to 1 wt % HMHEC solutions has overturned the trends in the viscosity–temperature relationship at certain temperature ranges. Similar opposite temperature patterns in rheology in systems containing nonionic cellulose ethers and ionic surfactants, SDS, or CTAB have been reported by Carlsson et al.<sup>13</sup> However, the celluloses used in their work have already shown a reverse viscosity–temperature relationship, in contrast to the normal pattern of our HMHEC. That is, the reverse temperature effects they observed may simply arise from the polymer itself, not conjointly from polymer and surfactant, which is reflected in our case.

It is worth mentioning that the surfactant–polymer solutions having 1 wt % HMHEC and various Tergitol 15-S-7 concentrations in this work show a typical flow behavior at low surfactant concentrations, viz., with viscosity reaching a maximum around 5 cmc's and then decreasing upon further addition of surfactant. Nevertheless, the crossovers between the viscosity vs shear rate curves of the HMHEC solutions with and without addition of surfactants have been observed, which is indicative of complex formation. To our limited knowledge, these kinds of observations have never been reported in the open literature. In this paper, we will give the details of our observations and our conjectures on the interaction mechanism will be discussed.

## 2. Experimental Section

**2.1. Materials.** 2-Hydroxyethyl cellulose (HEC) and hydrophobically modified 2-hydroxyethyl cellulose (HMHEC) were purchased from Aldrich. The HMHEC polymer with a mean molecular weight around 560K g/mol is hydrophobically modified with hexadecyl chains. The degree of ethyl substitution ( $DS_{\text{Ethyl}}$ ) is 2.0 per anhydroglucose unit, and the molar substitution of ethylene oxide groups ( $MS_{\text{EO}}$ ) ranges from 2.7 to 3.4 per anhydroglucose unit. No cloud point between 25 and 80 °C is observed in 0.5 wt % HMHEC solution. The HEC polymer with an average molecular weight of 720K g/mol was used in this work for comparison. All the information was provided by the supplier. Moreover, all the polymer concentrations investigated in this work were ensured to be higher than their overlap concentrations, obtained empirically from the complete Zimm plot using the static light scattering technique. Maestro et al.<sup>22</sup> also reported some other characteristics of HMHEC and HEC.

The commercial nonionic surfactant Tergitol 15-S-7 supplied by Union Carbide (USA) is a mixture of species with alcohol groups located at various positions along a chain of 11–15 carbon atoms and with an average ethylene oxide number of 7.3. The cloud-point value and pH value of 1 wt % Tergitol 15-S-7 micellar solution are around 37 °C and near 6.8. Its critical micelle concentration is as low as 39 ppm at 25 °C.<sup>35</sup> Deionized water from a Milli-Q purification system (Millipore) having a resistivity greater than 18.2 MΩ·cm was used in preparing samples and the mobile phase. All chemicals were used as received.

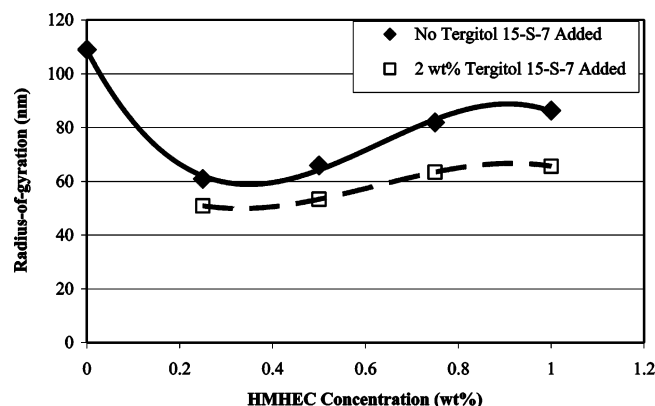
**2.2. Sample Preparation and Measuring Techniques.** A Haake RS 75 Rheostress rheometer equipped with the circulating water bath to control the variation of temperature within 0.1 °C was employed for the rheological measurements (Thermo Haake, Karlsruhe, Germany). Two different types of sensors, a double-gap cylinder sensor DG 41 and a cone-and-plate sensor, C35/1 (diameter = 35 mm and angle = 1°), were used accordingly. The DG 41 sensor was employed in measuring the steady-state shear viscosity and is able to provide a very good measurement of viscosity near that of water. However, owing to the design limit of the rheometer, the minimal shear rate had to be set at shear rates greater than ca. 10 s<sup>−1</sup> to ensure the reliability of our experimental results. In addition, the cone-and-plate sensor C35/1 (diameter = 35 mm and angle = 1°) was utilized to obtain the dynamic viscosity and the complex moduli. The stress-sweep tests were performed previously to ensure the small-amplitude oscillatory test in the linear viscoelastic regime. In measurements, the angular speed  $\Omega$  of the rotational cone as well as the corresponding torque  $T_o$  was recorded. The shear rate  $\dot{\gamma}$  and the shear stress  $\sigma$  could then be expressed in the following:

$$\sigma = \frac{3T_o}{2\pi R^3} \quad \text{and} \quad \dot{\gamma} = \frac{\Omega}{\tan \alpha} \approx \frac{\Omega}{\alpha} \quad (1)$$

where  $R$  and  $\alpha$  are the radius and the angle of the cone, respectively. Usually, the angle  $\alpha$  was less than 0.1 rad.

Viscosity measurements in some selected experiments were performed using capillary viscometers in a temperature-controlled water bath. Anhydrous glycerol and deionized water were used as references. No kinetic correction was applied, since the elution times of the samples were always greater than 6 min.

The radii of gyration  $R_g$  of the surfactant–polymer aggregates and the polymer itself were measured using the Brookhaven Light Scattering system equipped with a BI-200SM Geniometer,



**Figure 1.** Effect of Tergitol 15-S-7 on radii of gyration of HMHEC solutions at 25 °C.

an advanced BI-9000AT digital autocorrelator, and an argon ion laser at 514.5 nm (Model 95/2 Lexel). BIC-SLSW V2.09 software was employed to measure  $R_g$  at a specific polymer concentration, while BIC-Zimm software was utilized to obtain the Zimm plot, from which  $R_g$  at an infinite dilute condition was measured.

All the measurements were carried out at 25 °C, unless specified.

### 3. Results

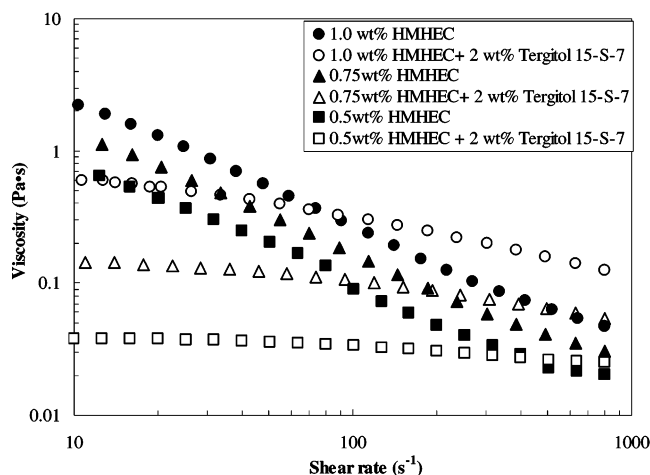
The overlap concentration  $C^*$  of the HMHEC polymer in water was evaluated with its measured radius of gyration,  $R_g$ , at an infinitely dilute condition using a complete Zimm plot. The  $R_g$  was found about 109 nm (Figure 1). Consequently, the overlap concentration of this HMHEC polymer is estimated to be around 0.17 g/L using the following approximation:<sup>10,33</sup>

$$C^* = \frac{M_w}{N_A[(4/3)\pi R_g^3]} \quad (2)$$

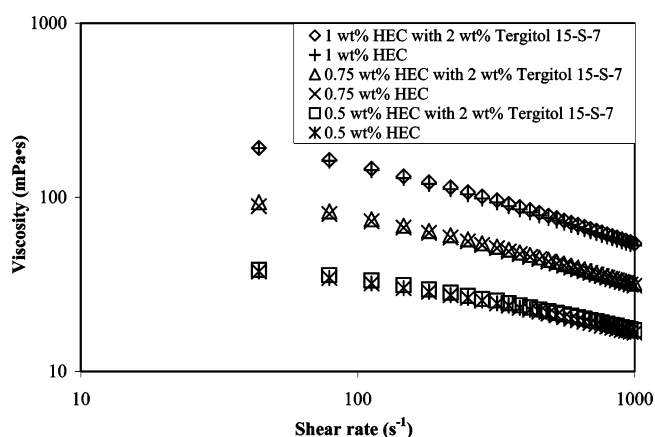
where  $N_A$  and  $M_w$  are Avogadro's number and the molecular weight of the polymer, respectively. This ensures that the concentration range of the HMHEC polymer, from 0.5 to 1 wt %, under investigation in this work is in the semidilute concentration regime.

Moreover, the concentration-dependent  $R_g$  of the polymer was measured as well using the same light scattering system but analyzed with BIC-SLSW V2.09 software. It indicates that the radii of gyration of the HMHEC polymer from 0.25 to 1 wt % are smaller than that in infinite dilute solution, and grow with increasing polymer concentration (Figure 1).

Tergitol 15-S-7 is known to form micelles in aqueous solutions at 25 °C, whose hydrodynamic radius is only 16 nm.<sup>35</sup> With addition of 2 wt % Tergitol 15-S-7 to HMHEC solution, it compacts polymer coils and, thus, leads to a decrease in  $R_g$  (Figure 1). The HMHEC–Tergitol 15-S-7 complexes, which are smaller than the HMHEC polymer itself, may stem from the amphiphilic nature of surfactant micelles and HMHEC polymer. The hydrophobic side chains of the HMHEC polymers could be brought more closely to the hydrophilic backbones of the polymers due to (1) the hydrophobic association between the hydrophobic cores of micelles and the hydrophobic side chains of polymer, and (2) the attractive interactions between the hydrophilic heads of micelles and the hydrophilic moieties on the HMHEC polymers. This will be discussed later in line with the necklace model.<sup>1,36</sup> Accordingly, the surfactant–polymer aggregates are expected to be stiffer.



**Figure 2.** Steady-state shear viscosity of HMHEC solutions with/without addition of 2 wt % Tergitol 15-S-7 surfactant at 25 °C.



**Figure 3.** Steady-state shear viscosity of HEC solutions with/without addition of 2 wt % Tergitol 15-S-7 surfactant at 25 °C.

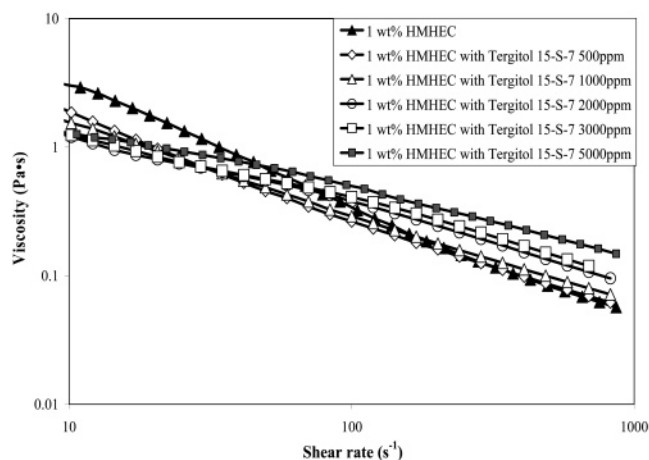
Interaction between HMHEC polymer and Tergitol 15-S-7 was studied rheologically as well. The steady-state shear viscosity curves of HMHEC solutions with/without addition of 2 wt % Tergitol 15-S-7 are shown in Figure 2. For comparison, similar measurements using 2-hydroxyethyl cellulose (HEC), instead, were performed and are exhibited in Figure 3.

Shear-thinning behaviors were observed in both HMHEC and HEC solutions (Figures 2 and 3). Addition of 2 wt % Tergitol 15-S-7 surfactant to the HEC solutions shifts the apparent viscosity curves slightly upward. Coincidentally, the viscosity increment is almost equal to the viscosity of the 2 wt % Tergitol 15-S-7 micellar solution, which exhibits a nearly Newtonian behavior and has a viscosity at 1.25 mPa·s.<sup>37</sup> This implies that no apparent interaction between surfactant and HEC polymer was observed. On the contrary, a very interesting shear-induced phenomenon was observed in HMHEC solutions.

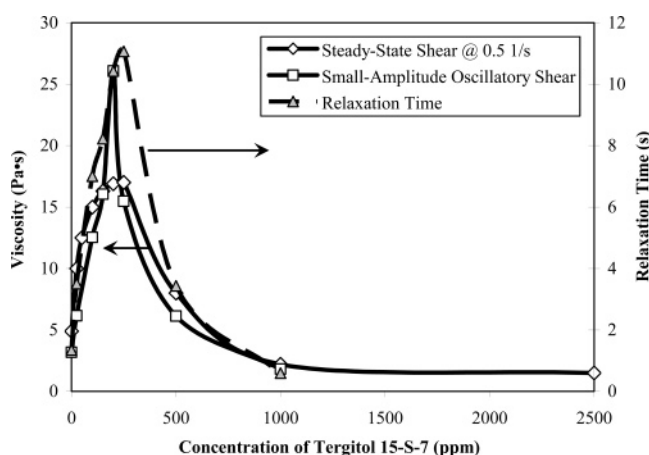
A crossover of the two steady-state shear viscosity curves for the HMHEC solution, i.e., with and without 2 wt % Tergitol 15-S-7 added, is clearly present. For example, in solutions containing 0.5, 0.75, and 1 wt % HMHEC, the crossovers took place at shear rates near 450, 185, and 75 s<sup>−1</sup>, respectively. That is, at a lower shear rate, the polymer solution poses a higher viscosity, whereas the surfactant–polymer solution is more viscous under a shear rate larger than that at the crossover.

To further examine such interesting phenomena, the steady-state viscosities of 1 wt % HMHEC solutions with added Tergitol 15-S-7 of various concentrations at 25 °C were measured and are presented in Figure 4. The surfactant





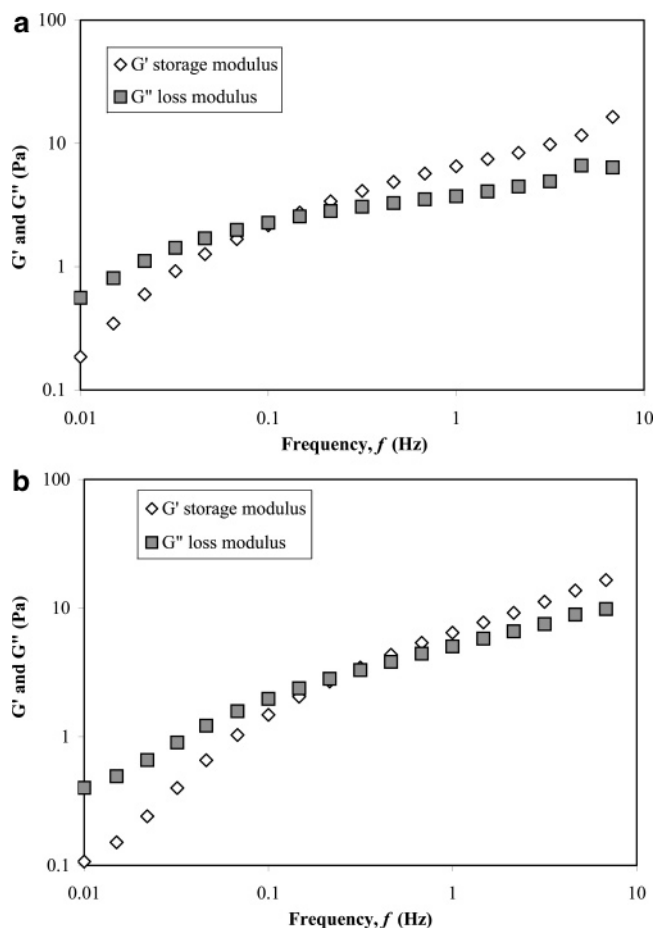
**Figure 4.** Steady-state shear viscosity of 1 wt % HMHEC solutions with/without added Tergitol 15-S-7 surfactant at 25 °C.



**Figure 5.** Low shear rate ( $0.5 \text{ s}^{-1}$ ) viscosity, zero shear viscosity, and characteristic relaxation times of 1 wt % HMHEC solution as a function of Tergitol 15-S-7 concentration at 25 °C.

concentration ranges from 500 to 5000 ppm, much greater than its cmc near 39 ppm.<sup>35</sup> Likewise, the crossovers between viscosity–shear rate curves were observed again. Fascinatingly, the crossovers drifted to a lower shear rate with more surfactant added.

Due to the limit of our rheometer, the steady-state shear viscosity only at a very low shear rate of  $0.5 \text{ s}^{-1}$ , instead of at the zero shear rate, is recorded. Figure 5 displays the viscosity of 1 wt % HMHEC solution at  $0.5 \text{ s}^{-1}$  as a function of Tergitol 15-S-7 surfactant concentration. It shows that the viscosity increases from  $4.9 \text{ Pa}\cdot\text{s}$  in pure 1 wt % HMHEC solution to a maximum value at  $17 \text{ Pa}\cdot\text{s}$  in the presence of 200 or 250 ppm surfactant, and then decreases sharply to  $1.5 \text{ Pa}\cdot\text{s}$  when more than 1000 ppm surfactant is present. This indicates that formation of intermolecular hydrophobic networks between nonionic surfactants and HMHEC polymer was enhanced with surfactant concentration less than 500 ppm, which could be attributed to (1) a strength increase in connections between the hydrophobic groups of HMHEC polymers and surfactant aggregates and (2) an increment in concentrations (or numbers) of such intermolecular hydrophobic junctions.<sup>8,30</sup> Moreover, information on different classes of interactions between polymers and surfactants, whether it is cooperative or noncooperative, can be identified from the measurements of the zero shear viscosities.<sup>1,8</sup> The cooperative association often occurs at a surfactant concentration far less than the cmc, whereas the noncooperative case, as in this work, happens at that above cmc.



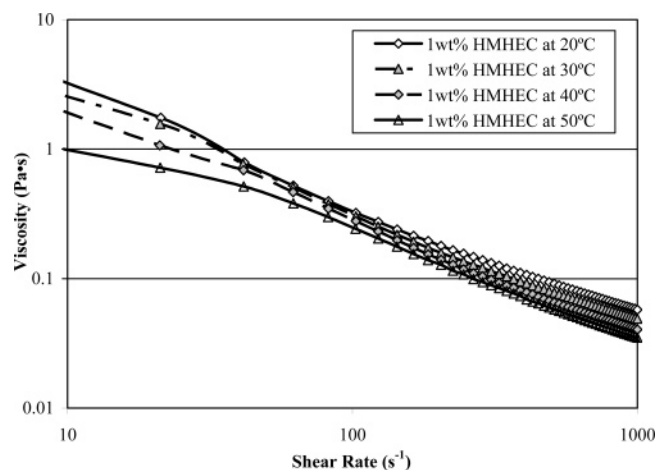
**Figure 6.** Storage ( $G'$ ) and loss ( $G''$ ) moduli for 1 wt % HMHEC solution at 25 °C: (a) without addition of Tergitol 15-S-7 surfactant; (b) with addition of 1000 ppm Tergitol 15-S-7 surfactant.

The low shear rate viscosity starts to decrease with the addition of more than 250 ppm Tergitol 15-S-7 and finally levels off at higher concentrations. With the concentration of added surfactant of more than 1000 ppm, the viscosity of the HMHEC–surfactant solution is even lower than that of pure HMHEC, which implies that the intermolecular hydrophobic network of HMHEC could have been weakened by the surfactant.

To further explore such trends, alternative measurements on the zero shear viscosity were conducted using small-amplitude oscillatory shear tests. Figure 6 shows typical plots of storage ( $G'$ ) and loss ( $G''$ ) moduli of 1 wt % HMHEC solutions at 25 °C with/without addition of Tergitol 15-S-7. We must note that, for the dynamic viscosity measurements, linear viscoelastic behavior was always ensured from prior stress-amplitude sweep tests. Consequently, a constant shear stress, 1 Pa, was chosen for the dynamic tests. With the small-amplitude oscillatory shear tests, the zero shear viscosity  $\eta_0$  can be approximated as a product of the characteristic modulus  $G^*$  and the characteristic relaxation time  $\tau$ .<sup>10</sup>

$$\eta_0 = G^* \tau \quad (3)$$

where the characteristic modulus is the modulus at the crossover in Figure 6, i.e.,  $G^* = G' = G''$ , and the characteristic relaxation time  $\tau$  is the reciprocal of the frequency in units of radian per second at the crossover. That is,  $\tau = 1/(2\pi f)$ , where  $f$  is given in hertz in Figure 6. Moreover, the characteristic relaxation time can be related to and sometimes regarded as the lifetime of the transient network as well.<sup>38</sup>



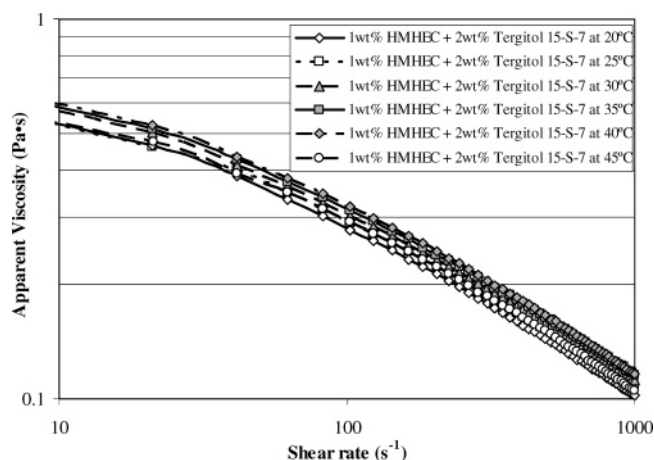
**Figure 7.** Effect of temperature on apparent viscosity of HMHEC solutions.

From the small-amplitude oscillatory shear measurements, the characteristic relaxation times and the zero shear viscosity estimated by eq 3 are plotted in Figure 5. Similar trends are shown between both viscosity–concentration curves, though the maximum viscosities differ. The zero shear viscosity reaches the maximum near 26 Pa·s, when 200 ppm Tergitol 15-S-7 surfactant is added, in contrast to 3.2 Pa·s in pure HMHEC solution measured by the same technique. Similarly, the characteristic relaxation time increases from 1.35 s in pure HMHEC solution to a peak near 11 s in the presence of 250 ppm surfactant, and then falls again to 0.6 s when 1000 ppm surfactant is added. When the concentration of added surfactant ranges from 200 to 250 ppm, saturation of surfactant binding to the temporary hydrophobic associate network may occur.<sup>38</sup> In a brief summary, Figure 5 shows that the steady-state viscosity at low shear rate ( $0.5 \text{ s}^{-1}$ ) largely coincides with that obtained from eq 3, except in the regime with the concentration of added surfactant ranging from 100 to 500 ppm, where the transient network forms between surfactant molecules and macromolecules are the strongest.

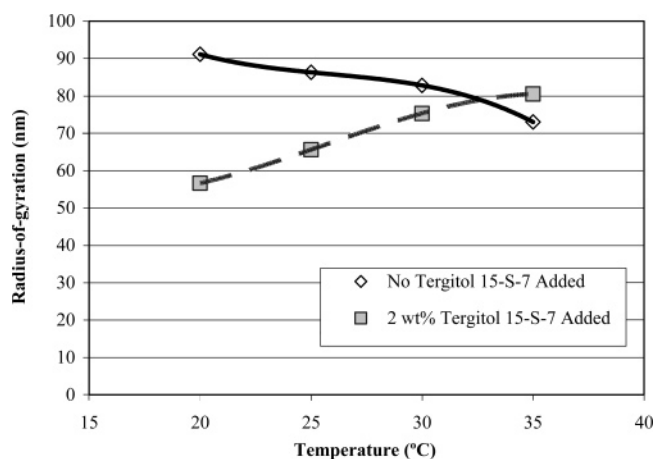
If significant hydrophobic interactions between the nonionic Tergitol 15-S-7 surfactants and the HMHEC polymers actually exist, alteration of the experimental temperature should have some profound influence on the system because the nonionic surfactants are very sensitive to changes of the temperature.<sup>39</sup>

An interesting phenomenon of the effect of temperature on the steady-state shear viscosity of the polymer solution in the presence of surfactant is observed and shown in Figures 7 and 8. Figure 7 just shows a usual temperature-dependent pattern in the viscosity of 1 wt % HMHEC solutions, which become more fluidic at elevated temperatures. In contrast, but noticeably, the presence of 2 wt % Tergitol 15-S-7 has reversed the trends in the temperature-dependent viscosity of 1 wt % HMHEC solutions. It increases with increasing temperature to about 40 °C, which is close to the cloud point of 2 wt % Tergitol 15-S-7 at 39 °C,<sup>35</sup> and drops significantly with a further temperature increment. Though not shown here, the Tergitol 15-S-7 micellar solutions still exhibit Newtonian behavior with viscosities near that of water at temperatures below their cloud points.

As aforementioned, Carlsson et al.<sup>13</sup> had previously reported their observation on the reverse temperature–viscosity pattern in their system. The HM polymers used by Carlsson et al.<sup>13</sup> had already shown a reverse behavior, in contrast to the normal pattern possessed by the HMHEC used in this work. Løyen et al.<sup>20</sup> also observed the formation of reversible thermal gelation, which gave a severalfold increment in viscosity. In their systems,



**Figure 8.** Effect of temperature on steady-state shear viscosity of 1 wt % HMHEC solutions with addition of 2 wt % Tergitol 15-S-7 surfactant.

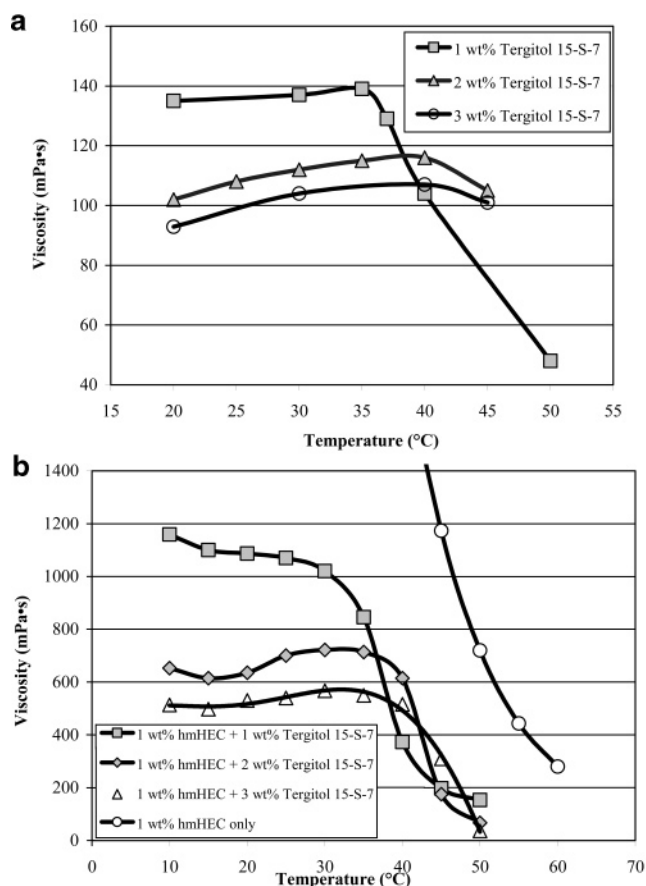


**Figure 9.** Effect of temperature on radii of gyration of 1 wt % HMHEC solutions.

the surfactant–HM polymer complexes go through a phase transition from the isotropic  $L_1$  micellar phase to various viscous lamellar liquid crystalline phases, with increasing temperature. That is, such a reverse trend in their systems mainly arises from the temperature-driven phase changes. In contrast, the complex solutions in our systems are all fluidic and show no birefringence under crossed polarizers.

Hydrophilicity of the polyoxyethylene (POE) surfactants mainly originates from the hydrogen bonding formation between ether oxygens on POE and free water molecules or hydrated hydrogens. That is, the number and strength of hydrogen bonds formed directly influence the hydrophilicity.<sup>26,39</sup> An increase in temperature causes the cleavage of such hydrogen bonds and, thus, dehydrates the surfactant. In other words, the hydrophobicity of POE surfactants increases with increasing temperature. The strength of the hydrophobic interactions and number of hydrophobic junctions between POE surfactants and HMHEC could be enhanced in this regard. However, bear in mind that another competing factor, Arrhenius behavior, also becomes more significant with increasing temperature.

Coincidentally, a significant growth of Tergitol 15-S-7–HMHEC aggregates and a decrease in  $R_g$  of HMHEC coils were observed (Figure 9). At 20 °C, addition of 2 wt % Tergitol 15-S-7 surfactant to 1 wt % HMHEC solution reduces the  $R_g$  from 91.1 to 56.6 nm, which accounts for 76% reduction in aggregate volume. Increasing the temperature from 20 to 35 °C, the radii of gyration of 1 wt % HMHEC decrease slightly from 91.1 to



**Figure 10.** Effect of temperature on viscosity of 1 wt % HMHEC solution: (a) at 1000 s<sup>-1</sup>; (b) near zero shear rate (from capillary viscometry).

80.5 nm. In contrast, the Tergitol 15-S-7–HMHEC aggregates grow rapidly from 56.6 to 80.5 nm in the same temperature range, ca. 300% enlargement in aggregate volume, which could be attributed to the sharp increase in aggregation numbers of surfactant micelles.<sup>35</sup> It is known that, in general, a larger aggregate tends to be more viscous. Thus, it is expected that the viscosity of the surfactant–polymer aggregates will increase during this temperature range.

However, the temperature effect becomes more subtle at temperatures around the cloud point, at which the water-depleted nonionic hydrophilic POE surfactants completely lose their water solubility and the micellar solution becomes turbid. When approaching the cloud-point temperature from below, the size and the aggregation numbers of Tergitol 15-S-7 increase sharply.<sup>35</sup> Though the HMHEC polymers are hydrophobically modified with hexadecyl chains, they are still not hydrophobic enough to induce clouding behavior at temperatures up to 80 °C.

Indeed, the 1 wt % HMHEC solutions with addition of 1, 2, or 3 wt % Tergitol 15-S-7 do not have discernible phase separation at 50 °C over a period of 2 days, though these complex solutions look very bluish. With a further increase in temperature to 60 °C, only that with 1 wt % surfactant segregates into a very clear top phase, occupying 20% of the overall phase volume, and a bottom phase similar to those observed at 50 °C. To avoid the nuisance arising from the phase separation affecting the viscosity measurements, the experimental temperature was set below 50 °C.

Figure 10 shows the effect of temperature on the viscosity of 1 wt % HMHEC solutions in the presence of Tergitol 15-

S-7 from capillary viscometry, i.e., near zero shear viscosity, and at a shear rate as high as 1000 s<sup>-1</sup>. In general, the viscosity increases slightly with increasing temperature and then drops sharply with a further increment in temperature. The onset of the sharp fall in viscosity is around 30 and 40 °C. Coincidentally, the cloud points of Tergitol 15-S-7 at these concentrations range from 35 to 40 °C.<sup>35</sup> It is noteworthy that the viscosity of 1 wt % HMHEC solution with Tergitol 15-S-7 added is smaller than that of pure 1 wt % HMHEC solution at the same temperature.

Moreover, the zero shear viscosity of 1 wt % HMHEC solution exhibits quite a good Arrhenius dependence on temperature<sup>10,19</sup> and gives the activation energy for hydrophobe disentanglement near 81.8 kJ/mol, comparable to that for other associative polymers.<sup>19</sup> In contrast, with addition of Tergitol 15-S-7, the viscosity of 1 wt % HMHEC solution changes. For instance, the viscosity of 1 wt % HMHEC solution having 1 wt % Tergitol 15-S-7 added decreases very slightly from 10 to 30 °C and then falls sharply from 30 to 50 °C. The Arrhenius plot shows two distinct regions, yielding activation energies of 4.04 kJ/mol at temperatures between 10 and 30 °C and 95.6 kJ/mol at temperatures ranging from 35 to 50 °C, respectively, for hydrophobe disentanglement.

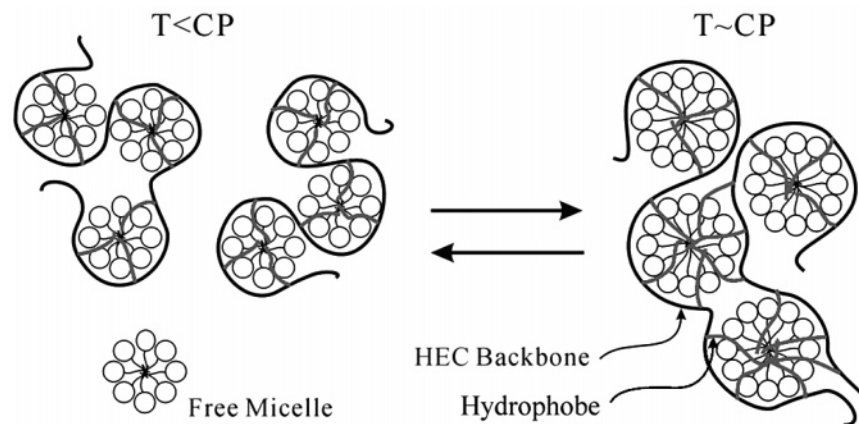
Interestingly, the reverse temperature dependence of the near zero shear viscosity is shown again with addition of 2 or 3 wt % surfactant to the 1 wt % HMHEC solutions from 15 to 35 °C. The increase in viscosity may be attributable to the increasing hydrophobicity of surfactant and, hence, the strength of hydrophobic interaction between HMHEC and surfactant. The following downturn in viscosity with temperature could be fitted well with the Arrhenius law, though the experimental temperature window may be too narrow to have more data points. However, the Arrhenius plot of the viscosity from 1 wt % HMHEC solution having 2 wt % Tergitol 15-S-7 still gives a very good linear fit with  $R^2 = 0.996$ , so that the activation energy is estimated at 186.9 kJ/mol. However, no positive activation energy could be obtained from the same solution at temperatures cooler than 35 °C, since the viscosity increases slightly with temperature.

#### 4. Discussion

The necklace model, shown in Figure 11, for the formation of polymer–surfactant complexes has long been proposed,<sup>1</sup> but only very recently confirmed using a sophisticated dielectric relaxation technique.<sup>36</sup> Moreover, Figure 5 implies that the hydrophobes of HMHEC at 1 wt % are saturated with Tergitol 15-S-7 at approximately 1000 ppm, i.e., 0.1 wt %. Hence, it is rational to infer that, in 1 wt % HMHEC solution having more than 1 wt % added surfactant, the bound micelles spatially appear in the HEC backbones of HMHEC and are in equilibrium with free micelles in excess in the bulk solution. The hydrophobes are preferentially solubilized in the hydrophobic cores of micelles, whereas some portions of the HEC backbone may encircle the bound micelles. Therefore, with more micelles bound to each polymer, the resulting surfactant–polymer complexes are smaller in size, as more portions of polymer chains wind around the micelles. That is, addition of surfactant could reduce the sizes of the complexes and, consequently, the viscosity (Figures 1 and 5).

Nonionic surfactant micelles are known to be dehydrated at elevated temperatures, because of the diminishing hydrogen bond formation. Accordingly, micelles are expanded. The nearby micelles, even those bound on different HMHEC macromolecules, tend to aggregate owing to dehydration, leading to larger aggregates. Under these circumstances, the intermolecular





**Figure 11.** Revised necklace model for interactions between HMHEC and Tergitol 15-S-7 in excess at temperatures below/near the cloud point (CP).

hydrophobic association among adjacent HMHEC macromolecules may occur again, schematically shown as Figure 11, because the micelles are large enough to house hydrophobes from different but adjacent HMHEC molecules. Again, a weak hydrogel is formed with these hydrophobic networks (Figure 9). Hence, the falling trend in the viscosity of the system may slow down or even upturn.

Moreover, the activation energy of hydrophobe dissociation could be regarded as the strength of the hydrophobic interaction among hydrophobes. Addition of enough surfactant, e.g., adding 1 wt % Tergitol 15-S-7 to 1 wt % HMHEC solution, could saturate or completely solubilize the hydrophobes, so that the interaction among hydrophobes is greatly screened. Consequently, a reduction in the activation energy of hydrophobe dissociation is expected, since not much hydrophobic association between polymers exists. For example, it is reflected on the very low or even nonexistent activation energy for hydrophobe disentanglements in 1 wt % HMHEC solution at temperatures below 35 °C, when more than 1 wt % Tergitol 15-S-7 is added. Likewise, the solution viscosities in such cases are relatively lower than that of pure HMHEC solution at the same temperature.

As mentioned previously, the intermolecular hydrophobic association among adjacent HMHEC macromolecules may occur again with a further temperature increment to the cloud point. The activation energy is expectedly larger and the Arrhenius dependence is counted again. Explicitly, two competing temperature effects on the solution viscosity in this HMHEC–Tergitol 15-S-7 system have to be accounted for. One is the common Arrhenius dependence, which reveals the decreasing viscosity against the increasing temperature. On the contrary, the expanding micelles owing to the clouding phenomena give again the possible formation of the intermolecular hydrophobic association, which increases the solution viscosity. However, the latter case is more complicated and is yet to be explored in more detail.

At temperatures higher than the cloud point of surfactant but still cooler than that in which macroscopic phase separation would occur in the bulk solution, no free micelles available in the bulk solution could contribute to the expansion of the bound micelles. Consequently, the solution viscosity simply follows the Arrhenius dependence and decreases with a further increase in solution temperature.

If the solution is further heated, phase separation in the complex solution will possibly take place. As mentioned previously, the 1 wt % HMHEC solution having 1 wt % Tergitol 15-S-7 does not undergo phase separation at 50 °C over a period

of 2 days, but forms a second liquid phase at ca. 60 °C. In such a biphasic system, though the slow phase separation kinetics is observed and the viscosity of the mixed solution is found to be very small, the viscosity data are not reliable. To ensure the reliability of our viscosity measurements, the experimental data reported herein are obtained at temperatures below 50 °C.

## 5. Conclusions

Rheological investigation on the interaction between neutral polymers, HMHEC or HEC, and the nonionic Tergitol 15-S-7 surfactant was carried out. Addition of Tergitol 15-S-7 at low concentrations increases the viscosity of HMHEC solution, which then decreases to a level even lower than that of the pure polymer solution with a further addition of surfactant. The viscosity maximum is found at about 5 cmc's, i.e., 200 ppm. However, no sign of interaction between HEC and the same surfactant is observed.

The steady-state shear measurements show that there exist crossovers between viscosity–shear rate curves of HMHEC solutions with and without surfactant added, whereas crossovers were not observed in the HEC–surfactant systems. Moreover, added Tergitol 15-S-7 reverses the effect of temperature on the viscosity of the HMHEC solutions or, specifically speaking, violates the Arrhenius dependence. That is, increasing the temperature to or near the cloud point raises the viscosity of the HMHEC–surfactant aggregates, in contrast to the viscosity decrease in the pure HMHEC solutions. In the HMHEC solution with surfactant in excess at a temperature far below the cloud point, the intermolecular hydrophobic association of HMHEC polymer is shielded with the excess micelles in bulk solution. Hence, the solution viscosity is expected to be lower. However, when the temperature is increased to that around the cloud point, the hydrophobic association, not only intramolecularly but also intermolecularly, is enhanced, as the expanded micelles may bridge again.

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