

Influence of Binary Surfactant Mixtures on the Rheology of Associative Polymer Solutions

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Hydrophobically modified alkali-soluble emulsion polymers (HASE) are a class of comblike associative polymers that can impart high viscosities to aqueous solutions. The rheology of HASE solutions can be tuned by the addition of surfactants, such as nonylphenol ethoxylates (NPe), where e is the length of the hydrophilic (ethoxylate) chain. While previous studies have considered individual surfactants, our focus here is on binary surfactant mixtures. We find that equimolar NP4–NP12 mixtures significantly enhance the zero-shear viscosities of HASE solutions as compared to equivalent amounts of NP8, especially at high overall surfactant concentrations. Dynamic rheological measurements suggest that the higher viscosities are due to increases in the lifetime of hydrophobic junctions in the polymer–surfactant network. In contrast to the above results, equimolar NP4–NP8 mixtures are rheologically identical to equivalent solutions of NP6. The differences between the two sets of mixtures are further correlated with cloud point measurements and thereby with the overall hydrophilic–lipophilic balance (HLB) of the surfactant system.

1. Introduction

Associative polymers, that is, hydrophilic polymers having hydrophobic pendant groups, are the rheology modifiers of choice in several applications including paints and coatings, personal care products, agrochemicals, enhanced oil recovery, and anti-icing aircraft fluids.^{1–9} Hydrophobically modified alkali-soluble emulsion (HASE) polymers are a class of associative polymers with hydrophobic alkyl groups grafted to the copolymer backbone in a comblike fashion. The hydrophobes associate in aqueous solution to form a transient network of hydrophobic junctions. This greatly enhances the solution viscosity and gives rise to other unique rheological properties. A large number of studies have been conducted on HASE polymers,^{10–18} with particular

focus on how their solution rheology is influenced by the polymer architecture (e.g., the hydrophobe size and side-chain length)^{19–21} or by the addition of surfactants. Surfactants can associate with the hydrophobes and can thus vastly alter the dynamics and rheology of HASE solutions. Interestingly, the viscosity has been observed to increase, decrease, or exhibit a maximum, depending on the surfactant concentration and type.^{12,14,22–25}

Recently,²³ we examined the addition of nonylphenol polyethoxylate (NPe) nonionic surfactants to HASE solutions. The hydrophilic lipophilic balance (HLB) of the NPe's was varied by using surfactants with differing numbers of ethoxy units ($e = 6, 8, 12,$ and 15). In the case of NP8, NP12, and NP15 (relatively high HLB), the zero-shear viscosity of the HASE/NPe solutions exhibited a maximum in viscosity as a function of the surfactant concentration (the data are replotted in Figure 1). On the other hand, the NP6 surfactant (low HLB) increased the viscosity monotonically over the concentration range studied (Figure 1). The results were explained as follows: at low concentrations, the surfactant molecules enhance the number as well as strength of hydrophobic junctions between the HASE chains. At higher concentrations, the NP8, NP12 and NP15 form micelles, which envelop the polymer hydrophobes, making their participation in junctions ineffective and thereby lowering the viscosity. Only a monotonous viscosity increase is observed for NP6 because this surfactant has a weak tendency to form micellar structures.

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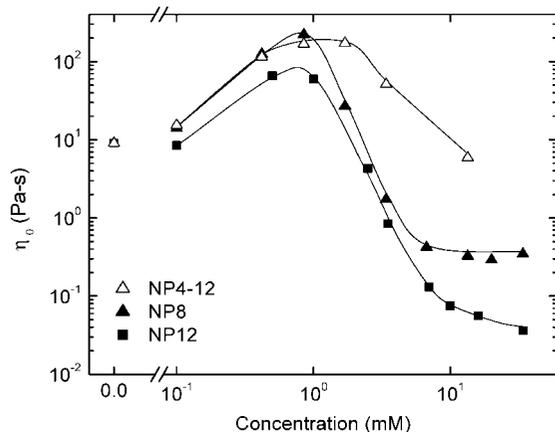


Figure 3. Low shear viscosity (η_0) of 0.5% HASE/NP surfactant systems as a function of surfactant concentration. NP4–12 denotes an equimolar mixture of NP4 and NP12.

All rheological experiments were performed at pH = 9 and $T = 25^\circ\text{C}$ using a TA Instruments AR-2000 stress-controlled rheometer fitted with a cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. Because the steady shear response of HASE polymer/surfactant systems is sensitive to shear history, a preshear was applied at a strain rate of 5 s^{-1} for 180 s followed by a rest period of 120 s. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime, which was thereafter utilized to perform the dynamic frequency sweep test. Zero or low-shear viscosity was determined from the steady shear viscosity profiles by averaging over the first 10 points of the Newtonian region. Each experiment reported in this study was performed at least twice, and all experiments were reproducible within $\pm 5\%$. The error is included in the symbol size.

Cloud point temperatures were determined visually as the temperatures at which clear or slightly hazy surfactant solutions turned opaque on heating and clear on subsequent cooling. Each measurement was done thrice to ensure accuracy.

3. Results and Discussion

3.1. Equimolar Surfactant Mixtures. We first studied mixtures of NP4 and NP12 combined with 0.5 wt % HASE solutions. On the basis of the results in Figure 1, we expect NP4 and NP12 to exhibit entirely different trends on viscosity, that is, a monotonic increase for NP4 versus an increase followed by a decrease for NP12. Because equimolar NP4–NP12 mixtures are equivalent to NP8 in terms of the average EO chain length, we also study NP8 for comparison purposes. Figure 3 plots the zero-shear viscosity as a function of overall surfactant concentration for: (a) equimolar mixture of NP4–NP12, (b) NP8, and (c) NP12. We did not measure the rheology of NP4/HASE mixtures because these samples were inhomogeneous even at low NP4 concentrations (NP4 alone is insoluble in water). For the same reason, we were able to study equimolar NP4–NP12 mixtures with HASE only up to an overall surfactant concentration of 13.6 mM. The results in Figure 3 show a trend for NP4–NP12 that is qualitatively similar to NP8, that is, an increase in viscosity up to a maximum followed by a decrease. The two curves overlap at low surfactant concentrations up to ca. 0.85 mM. Thereafter, two differences are observed: first, the viscosity maximum for NP4–NP12 occurs at a slightly higher surfactant concentration than that for NP8. Second, beyond the viscosity maximum, NP4–NP12/HASE samples still exhibit almost an order-of-magnitude higher viscosity than the equivalent NP8/HASE samples. Thus, with respect to HASE solution rheology, there is clearly a synergism between NP4 and NP12 at high surfactant concentrations.

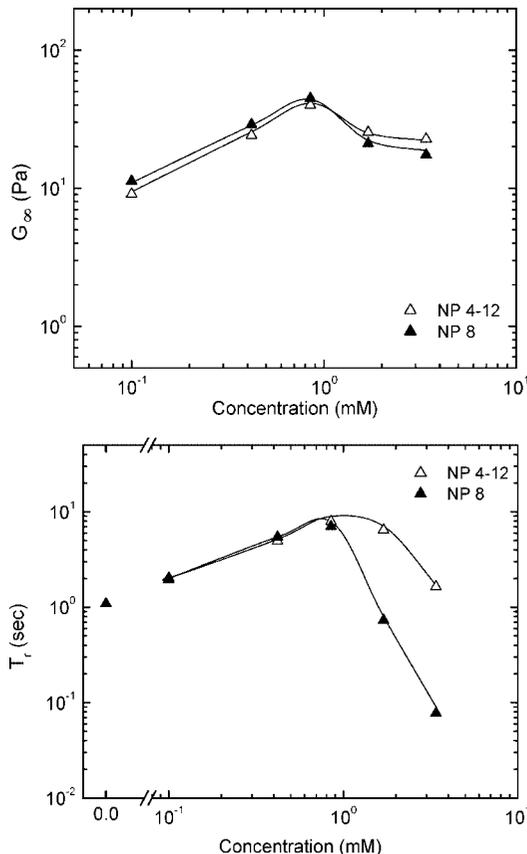


Figure 4. Plateau modulus G_∞ (a) and characteristic relaxation time T_r (b) as a function of NPe ($e = 4, 8,$ and 12) surfactant concentration (C_{NPe}) for 0.5% HASE polymer/NPe surfactant systems. NP4–12 denotes an equimolar mixture of NP4 and NP12.

We further probed the rheology of NP4–NP12/HASE mixtures using dynamic rheology. From the frequency spectra, that is, plots of the elastic modulus (G') and viscous modulus (G'') versus angular frequency ω , we obtained two parameters: G_∞ and T_r . T_r is the longest characteristic relaxation time of the solution and is given by the inverse of the frequency at the intersection between the G' and G'' curves. Although the relaxation time obtained in this manner is applicable to Maxwell-type viscoelastic behavior, which is not obeyed by our samples, nonetheless the values obtained from this treatment should be adequate for comparison purpose. The utility of T_r is that it provides an estimate for the lifetime and thereby the strength of hydrophobic junctions.²² G_∞ , on the other hand, is the high-frequency value of G' , that is, the plateau modulus. It is proportional to the number density of mechanically active hydrophobic junctions.³² G_∞ is defined only for samples exhibiting a plateau in G' , and we estimate it as the value of G' at a frequency of 25 rad/s, as has been done previously.^{22,23}

Figure 4a and b shows plots of G_∞ (density of hydrophobic junctions) and T_r (lifetime of junctions), respectively, for NP4–NP12/HASE and NP8/HASE. We observe from Figure 4a that G_∞ is practically identical for the two cases across the range of surfactant concentrations. On the other hand, Figure 4b shows that T_r at high surfactant concentrations is significantly greater for the NP4–NP12/HASE than the NP8/HASE one. The shape of the T_r plot mirrors that of the viscosity plot (Figure 3), indicating that the synergism observed with NP4–NP12 mixtures is due to increases in relaxation time. As mentioned, a higher T_r implies

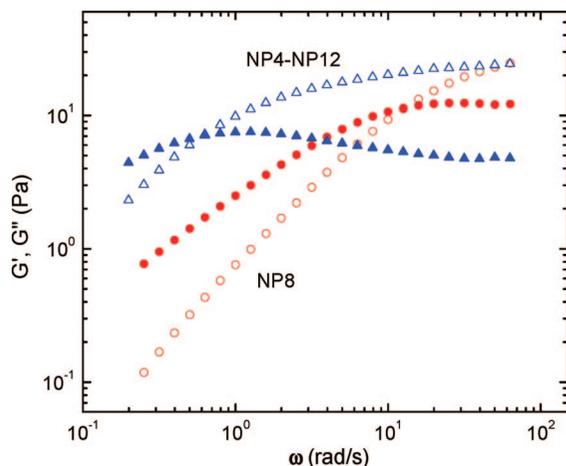


Figure 5. Variation of G' (unfilled symbols) and G'' (filled symbols) as a function of ω in 0.5 wt % HASE solutions containing 3.4 mM NP8 (circles) and 3.4 mM NP4-NP12 (1:1 molar ratio).

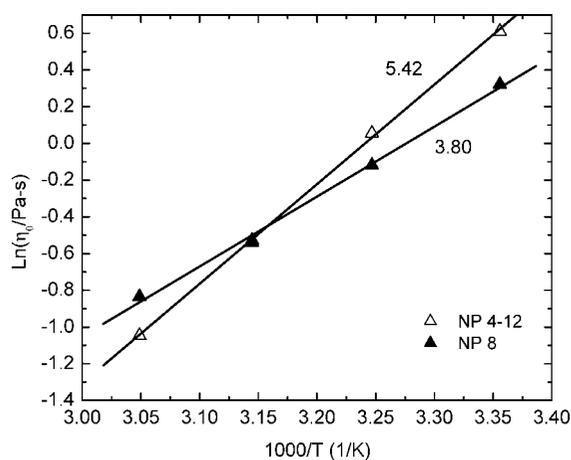


Figure 6. Arrhenius plots of zero shear viscosity of 0.5 wt % HASE polymer with 5 mM surfactant concentrations.

an increase in junction lifetime; that is, hydrophobic junctions are more tightly held together in the case of the surfactant mixture. To further underscore the differences in rheological response between the NP4–NP12/HASE and NP8/HASE samples, we show the full dynamic frequency spectrum in Figure 5 for samples at an overall surfactant concentration of 3.4 mM. Note that the plateau moduli are comparable, whereas the G' – G'' intersection occurs at a significantly lower frequency (i.e., longer time scale) for the mixture. In other words, the mixture shows a strong viscoelastic response whereas the NP8 sample shows a predominantly viscous response.

Further insight is obtained by studying the effects of temperature on the above solutions. From these experiments, the activation energy E_a can be obtained. E_a is a measure of the energy required for the hydrophobic junctions to dissociate,²⁵ in other words, it is another measure of junction strength. E_a values can be calculated from plots of the zero-shear viscosity η_0 versus $1/T$ using the Arrhenius equation:

$$\eta_0 = A_{\text{exp}} \exp(E_a/RT) \quad (3)$$

where A is the Arrhenius constant and R is the gas constant. Figure 6 shows Arrhenius plots for 0.5 wt % HASE solutions with NP4–NP12 and NP8 at a relatively high surfactant concentration of 5 mM. In both cases, the data fall on a straight line and the values of E_a calculated from the slopes are: 45 kJ/

mol for NP4–NP12 and 31.6 kJ/mol for NP8. The higher value of E_a for the mixture again suggests that the hydrophobic junctions are packed tighter in this case.

How can we explain the synergism in NP4–NP12 mixtures at high surfactant concentrations? As noted earlier, the type of aggregate formed by surfactants in water is governed by molecular geometry and expressed in terms of the packing parameter P . NP12 and NP8 surfactants are known to form spherical micelles in water, suggesting that $P \approx 1/3$ in those cases. On the other hand, NP4 is only sparingly soluble in water, and its significantly smaller headgroup area a_0 suggests that it has a significantly larger P . We can therefore expect mixtures of NP4–NP12 to have a lower effective hydrophilic group area a_0 as compared to NP8 and thereby a higher P . The lower a_0 is essentially due to reduced steric hindrance between the EO head groups when there is a difference in their sizes. The net result is an increase in P for the mixture from 1/3 to ca. 1/2, which would drive a transition from spherical to rodlike mixed micelles.

What consequences would a transition from spherical to rodlike micelles have on HASE rheology? Spherical micelles tend to envelop polymer hydrophobes, as shown in Figure 7a. Because surfactants exchange rapidly between spherical micelles, these micelles have a rather short lifetime before they break apart and reform. Thus, the micelles lower the lifetime of network junctions, and, in turn, the solution viscosity will be significantly lowered. Rodlike micelles, on the other hand, are long enough to interact with hydrophobes on a larger number of adjacent chains (Figure 7b), which means that it is more difficult to disengage from a junction.³³ The lifetime of a rodlike micelle is also much higher than that of a spherical micelle. Thus, the presence of rodlike micelles at high surfactant concentrations does not appreciably decrease the lifetime of network junctions. The viscosity still goes through a maximum, corresponding to the onset of micellization; however, there is only a moderate decrease in viscosity thereafter. (We should point out that NP4–NP12 micelles are not long enough to increase viscosity on their own; that is, these micelles are not wormlike chains.³⁴ This is confirmed by rheological studies on NP4–NP12 mixtures in the absence of HASE, which do not show any discernible viscoelasticity over the concentrations studied.)

We now consider a different NP e surfactant mixture where we see a different trend. These are equimolar mixtures of NP4 and NP8, and we compare their effects to that of the equivalent NP6. Results with 0.5% HASE for the zero-shear viscosity versus surfactant are shown in Figure 8. Here, the trends as well as individual values of the viscosity are nearly identical for NP4–NP8 and NP6. In both cases, there is an initial increase followed by a region of near-constant viscosity (whereas for NP8 alone, there is a maximum in the viscosity). Figure 9a and b shows the plots of G_∞ and T_r , respectively, for the above systems with increasing surfactant concentration. Again, the data are virtually identical for the two systems. Indeed, the overall frequency spectra were also virtually identical for NP4–NP8 and NP6 at a given surfactant concentration (data not shown). In other words, there is no discernible rheological synergism in mixtures of NP4 and NP8 with HASE. Evidently, the EO chain lengths are too similar in this case to cause significant differences in micellar structure.

3.2. Mixtures at Various Surfactant Ratios. Next, we consider mixtures of NP6 and NP12, where we can systematically study the effect of surfactant ratio on HASE solution rheology. (This could not be done for NP4-containing mixtures because

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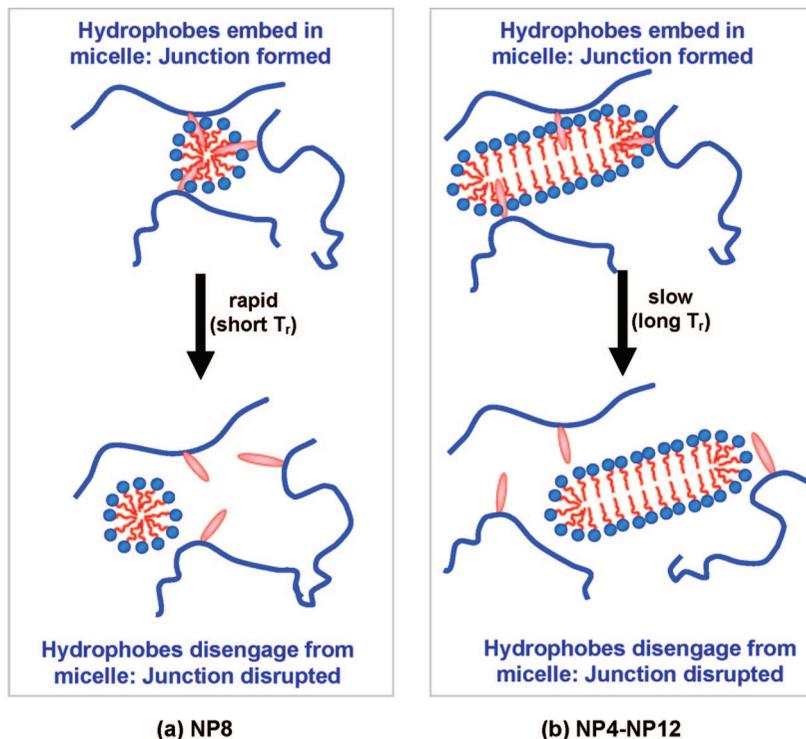


Figure 7. Schematics showing the micellar structure and polymer–micelle interaction in HASE–surfactant mixtures. (a) In NP8/HASE, the micelles are spherical and the polymer hydrophobes disengage from the micelles rapidly. (b) In equimolar NP4–NP12 mixtures, the micelles are rodlike and the polymer hydrophobes disengage much more slowly from the micelles. The junction lifetime is therefore much larger and so is the relaxation time.

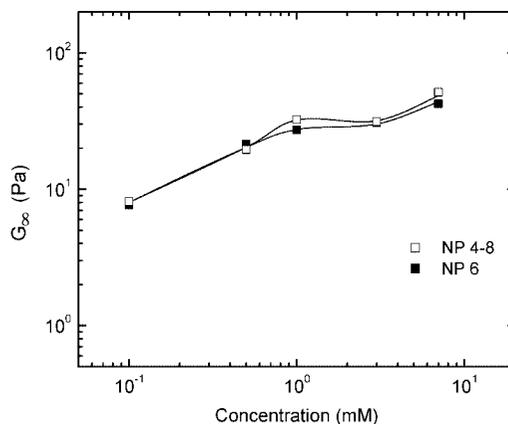
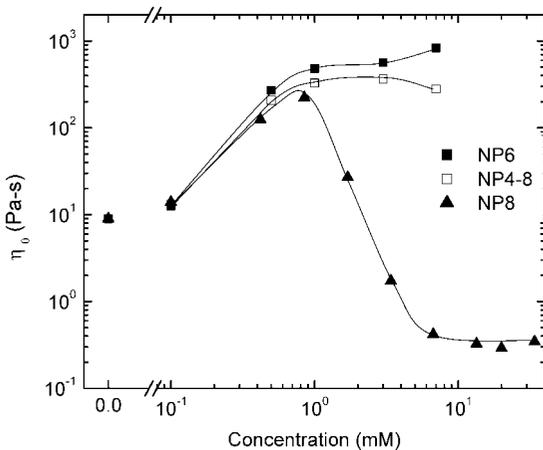


Figure 8. Low shear viscosity (η_0) of 0.5% HASE/NP surfactant systems as a function of surfactant concentration. NP4–8 denotes an equimolar mixture of NP4 and NP8.

NP4 itself was quite insoluble in water.) Figure 10 shows the plots of low-shear viscosity versus surfactant concentration for different NP6:NP12 molar ratios (1:0, 6:1, 3:1, 2:1, 1:1, 0:1) in a 0.5% HASE solution. Note that NP12 alone increases the viscosity up to a maximum followed by a decrease below the initial HASE viscosity, while NP6 alone causes a monotonic rise in viscosity up to a near-plateau. Interestingly, NP6–NP12 mixtures show trends similar to those of NP12, that is, viscosity peaks at low or moderate NP6:NP12 ratios (3:1, 2:1, 1:1). It is only at a molar ratio of 6:1 NP6:NP12 that the viscosity does not show a dip and instead levels off at high concentrations. At all ratios, the viscosity values are nearly identical up to the maximum (~ 0.5 mM surfactant), and thereafter the curves begin to diverge. At high surfactant concentrations, the viscosity steadily increases with an increase in NP6 content in the mixture.

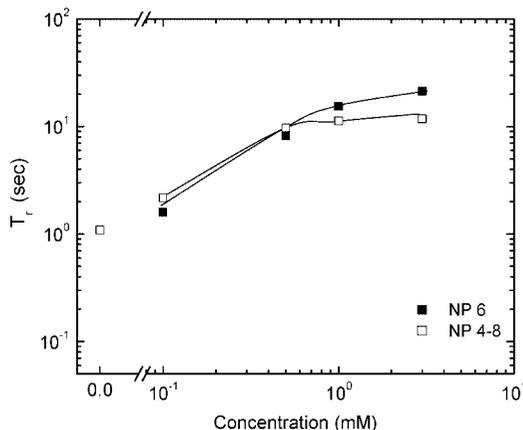


Figure 9. Plateau modulus G_∞ (a) and characteristic relaxation time T_r (b) as a function of NPe ($e = 4, 6, \text{ and } 8$) surfactant concentration (C_{NPe}) for 0.5% HASE polymer/NPe surfactant systems. NP4–8 denotes an equimolar mixture of NP4 and NP8.

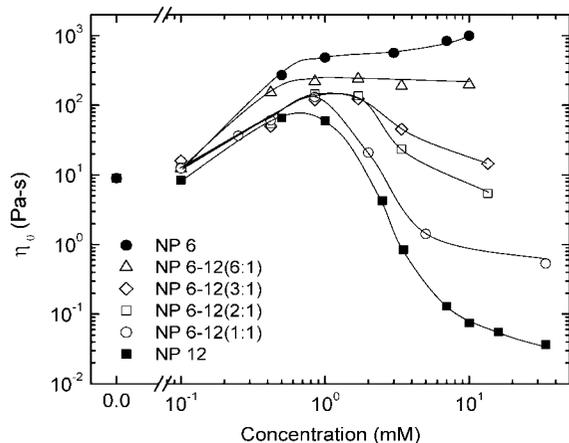


Figure 10. Low shear viscosity (η_0) of 0.5% HASE/NP surfactant systems as a function of surfactant concentration for different ratios of NP6–P12 mixtures.

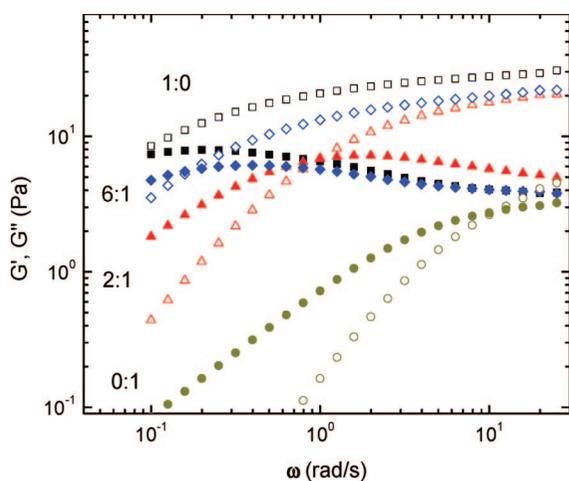


Figure 11. Variation of G' (unfilled symbols) and G'' (filled symbols) as a function of ω in 0.5 wt % HASE solutions containing 3.4 mM NP6–NP12 at different molar ratios.

We also conducted dynamic frequency spectra on NP6–NP12 mixtures. Data at 3.4 mM overall surfactant are shown in Figure 11. We observe an increase in both plateau modulus (G_∞) as well as characteristic relaxation time (T_r) with increasing NP6 content. The results imply an increase in both the density and the lifetime of network junctions with increasing NP6 fraction. Again, a sensible microstructural interpretation is that the addition of NP6 to NP12 induces a transition from spherical to cylindrical micelles. These micelles will have longer lifetimes than spherical NP12 micelles, and accordingly the network junctions in HASE solutions will also be longer lived. Furthermore, as has been mentioned earlier (cf., Figure 7), at high concentrations, spherical micelles would have a greater adverse effect on junction density than cylindrical micelles.

3.3. Surfactant Mixtures and Cloud Points. Finally, we consider a simple parameter that can be used in evaluating

Table 2. Cloud Point Temperatures of 1 wt % NPe Surfactants and Their Mixtures in Water

surfactant mixture	cloud point (°C)	individual surfactant w/equivalent EO	cloud point (°C)
NP4–NP8 (1:1)	<0	NP6	<0
NP4–NP12 (1:1)	23	NP8	43
NP6–NP12 (1:1)	36	NP9	54
NP6–NP12 (2:1)	16	NP8	43

nonionic surfactant mixtures for possible synergistic effects. Ethoxylated nonionic surfactants are known to show cloud point behavior. The cloud point temperature (CPT) is the temperature at which the surfactant solution becomes cloudy upon heating. The clouding occurs due to the dehydration of EO groups with increasing temperature. Table 2 shows the CPTs of 1 wt % NPe ($e = 6, 8, \text{ and } 9$) surfactants in water. We see that the CPT of NPe surfactants increases with increasing EO length, that is, with increasing hydrophilicity or HLB.^{26,35} Also shown in Table 2 are the CPTs of different mixtures of surfactants equivalent in EO chain length to the individual surfactants. We observe that the CPT for an equimolar mixture of NP4 and NP12 (23 °C) is 20 °C lower than the CPT of NP8. In other words, the mixture acts like a surfactant with lower HLB when compared to the analogous individual surfactant. Similar results are observed for mixtures of NP6 and NP12 at different ratios, when compared with individual NPe surfactants with equivalent EO chain length. These results are consistent with our idea that the mixtures are effectively equivalent in terms of microstructure formation to an individual surfactant that is more hydrophobic (lower HLB or higher packing parameter).

4. Conclusions

In this study, we examined the effect of nonionic surfactant mixtures on the rheology of a comblike associative polymer and compared it to that of analogous individual surfactants with equivalent hydrophilic chain lengths. The addition of NP4–NP12 surfactant mixtures, as opposed to NP8, to the associative polymer leads to considerably higher values of viscosity at high surfactant concentrations. On the other hand, NP4–NP8 mixtures do not exhibit any significant difference in viscosity trends when compared to equivalent NP6 surfactant. The observed behavior is explained in terms of transition in micellar structure due to difference in hydrophilic chain lengths in surfactant mixtures and is supported by the dynamic rheological results and activation energy data. The ratios of surfactants in binary mixtures are also shown to have a profound effect on the trends of viscosity with increasing concentration. Cloud point measurements further support our hypothesis that, in cases where the difference in surfactant hydrophilic chain length is large, surfactant mixtures behave similar to a surfactant with lower HLB when compared to the analogous individual surfactant.

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