

Surfactant-Mediated Modulation of Hydrophobic Interactions in Associative Polymer Solutions Containing Cyclodextrin

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The ability of nonionic surfactants to modulate the rheological characteristics of comblike hydrophobically modified associative polymer solutions containing cyclodextrin (CD) is examined. Addition of either α - or β -CD to these polymers results in a marked decrease in solution viscosity and viscoelastic properties because of the encapsulation of the polymer hydrophobes by CD. Nonionic surfactants, introduced to such a system, alter the hydrophobic interactions by competing with the polymer hydrophobes for complexation with the CDs. In this regard, nonylphenol ethoxylates (NP e) with different ethylene oxide chain lengths, which determine the hydrophilic–lipophilic balance (HLB) of the surfactant, are used. Our results reveal that the extent and rate of recovery of zero shear viscosity as well as dynamic moduli are strongly influenced by the type of CD (α versus β) as well as the HLB of the surfactant. For polymer solutions containing α -CD, recovery is observed solely in the presence of a low-HLB surfactant (NP6 and NP8). Additionally, in the case of NP6, the viscosity increases monotonically above the original hydrophobically modified alkali-soluble emulsion viscosity with surfactant addition, whereas for that of a higher HLB surfactant (NP15), the viscosity shows no appreciable change. In the case of β -CD, on the other hand, a complete recovery as well as further enhancement of rheological properties is achieved using the above surfactants. However, the trends of viscosity modulation are dissimilar for different surfactants as we witness a monotonous increase in the case of NP6 while a maximum in viscosity is observed in the presence of NP8 and NP15. The contrasting observations can be explained in terms of varying affinities of α - and β -CDs to bind with NP surfactants and the existence of different micellar structures in solution as governed by surfactant HLB. These results are further confirmed by UV/vis spectroscopy and cloud point measurements.

1. Introduction

Hydrophobically modified associative polymers are water-soluble polymers that have drawn considerable research attention owing to their unique thickening mechanism which renders them useful in several industrial applications such as aircraft anti-icing fluid,¹ paints and coatings,² and personal care products.³ These polymers possess hydrophobic groups grafted onto their backbones either at the ends or in a comblike fashion.^{4–9} One class of such comblike associative polymers are hydrophobically modified alkali-soluble emulsions (HASEs) that contain pendant hydrophobic groups which interact in aqueous solution to form a transient physical network consisting of both intra- and

intermolecular hydrophobic junctions.^{4,10–13} The presence of these junctions imparts distinctive rheological characteristics to these solutions including enhanced solution viscosity and a pronounced shear thinning behavior.⁴

From an application standpoint, it is at times desirable to deactivate the hydrophobic associations at one stage, thereby reducing the solution viscosity, and then “reactivate” them at a later stage, thus recovering the viscosity. Hydrophobic interactions in HASE polymers can be controlled to a certain extent by varying different parameters such as the ionic strength¹³ and pH,⁸ and addition of surfactants.^{10,14–16} However, a complete reversal of the associative behavior of these polymers cannot be accomplished by varying these parameters. An effective route to deactivate the hydrophobic associations in such systems is to use cyclodextrins.^{17–22} Cyclodextrins are doughnut-shaped cyclic oligosac-

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charides composed of α -D-glucopyranose units and have a hydrophilic exterior and a nonpolar inner cavity. Depending on the number of glucose rings, there are three types of naturally occurring cyclodextrin; α -, β -, and γ - cyclodextrin having six-, seven-, and eight-membered rings, respectively. Studies dealing with the inclusion complexes of CDs with a variety of organic and inorganic guest molecules in solution have been widely reported in several papers.^{23–27} Previous studies from our group^{18,20} reveal that both α - and β -CDs drastically affect the rheology of HASE polymers. The inner hydrophobic cavity of CD encapsulates the pendant hydrophobic groups, resulting in a disruption of hydrophobic associations, which translates into reduction in both viscosity and viscoelastic properties of polymer solutions by several orders of magnitude. The encapsulation of hydrophobic segments by CDs has been confirmed by ¹H NMR, differential scanning calorimetry, and thermogravimetric analysis. Furthermore, it has been verified that CDs do not interact with the water-soluble HASE backbone.¹⁸

A unique feature of CD–hydrophobe complexation in associative polymers is the recovery of hydrophobic associations that can be achieved by using surfactants that have a stronger affinity to bind with CDs as compared to the polymer hydrophobes. Despite the importance of such systems, very few studies have explored the utility of surfactants in recovering the solution rheology of hydrophobically modified associative polymers in the presence of cyclodextrin.^{17,18} Abdala et al.¹⁸ did some initial work on exploring the scope of viscosity recovery in HASE polymer solutions containing β -cyclodextrin by using two different nonionic surfactants. They found that the addition of surfactant to the solution leads to a near complete recovery of the viscoelastic properties. Similar viscosity recovery was observed upon addition of sodium dodecyl sulfate (SDS) in solutions containing hydrophobically modified poly(acrylic acid) wherein the hydrophobic groups were completely masked by α -cyclodextrin.¹⁷

An important aspect to be considered here is that changing the amphiphilicity of the nonionic surfactant employed is expected to influence the viscosity recovery to a large extent. This hypothesis is based on two suppositions. First, surfactant amphiphilicity, as measured by its hydrophilic–lipophilic balance (HLB), is an important factor that affects the binding affinity of a surfactant with cyclodextrin. For the case of nonionic surfactants, HLB is generally defined as

$$\frac{M_H}{M_H + M_L} \times 20 \quad (1)$$

where M_H is the molecular weight of the hydrophilic portion of the surfactant molecule and M_L is the molecular weight of the hydrophobic or lipophilic portion.²⁸ A higher HLB value thus indicates higher water solubility and a higher critical micelle concentration (cmc) and vice versa. Eli et al.²⁹ studied the effect of nonionic surfactant HLB on the association constant between triblock polyether nonionic surfactants and β -CD. They reported

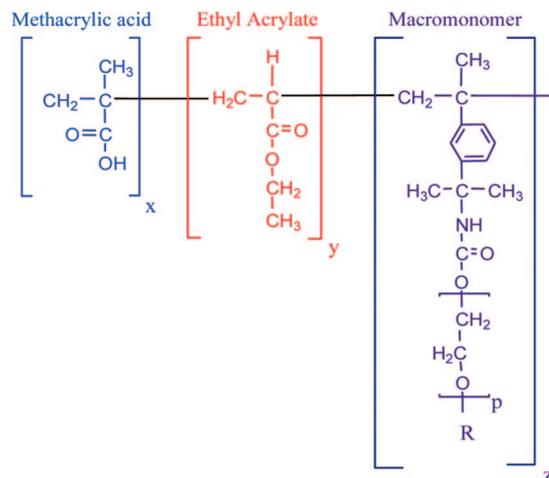


Figure 1. Molecular structure of the model HASE polymer. R = C₂₂ alkyl chain polymer hydrophobe, P = 40 EO poly(ethylene oxide) spacer, and $x/y/z = 43.57/56.21/0.22$.

that the smaller the HLB values of the nonionic surfactant, the greater the association constant with β -CD. This is intuitive as a smaller value of HLB would imply a relatively more hydrophobic surfactant and hence a stronger association with the hydrophobic cyclodextrin cavity. The second supposition is derived from the influence of the surfactant HLB on the polymer–surfactant interaction. In a previous study on the interactions between HASE polymer and nonionic surfactants having the same hydrophobic tail but varying lengths of the hydrophilic head, the authors highlighted the role of the HLB of nonionic surfactant in hydrophobic associations in solution.¹⁵ Depending on the HLB of the surfactant and its concentration, different trends of the rheological properties of the associative polymer in solution are observed. These considerations make it meaningful to examine the role of surfactants with different HLBs on the recovery of rheological characteristics in associative polymer solutions containing cyclodextrin.

In the present study we explore the effect of surfactants with different HLBs on the recovery of viscoelastic properties of HASE solutions in the presence of either α - or β -cyclodextrin. To the best of our knowledge, no work on the interaction of HASE/cyclodextrin systems with different HLB surfactants has been reported in the scientific literature. The surfactants used in this study are part of a homologous series of nonylphenol ethoxylate (NPe) surfactants, where e denotes the average number of hydrophilic ethylene oxide (EO) groups in the surfactant molecule. We first examine the effect of the surfactant concentration on the steady state as well as the dynamic rheological behavior of HASE solutions in the presence of either α - or β -cyclodextrin. We then explore the role of varying surfactant HLBs in the rheological response in these systems. Finally, to address the apparent differences in the behavior of α - and β -CD, we compare cloud point phenomena of both pure surfactant solutions and polymer/surfactant systems in the presence of different types of cyclodextrin.

2. Materials and Methods

The model HASE polymer used in this study was obtained from UCAR emulsion systems (Dow Chemicals, Cary, NC) in the form of aqueous latex at a solid concentration of approximately 26 wt %. A schematic of the chemical structure of the HASE molecule is shown in Figure 1. The macromonomer is composed of a poly(ethylene oxide) (PEO) spacer with an average number of EO groups equal to 40 mol and a C₂₂ alkyl group which is linked to the

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backbone through a urethane linkage. Details about the protocol to purify and prepare the polymer solution can be found in previous papers.^{10,15,30,31} The pH of the subsequently prepared polymer solution was adjusted between 9 and 9.5 by adding 0.1 M NaOH. The ionic strength of the samples was adjusted to 0.05 M NaCl to contain any polyelectrolyte effect.³¹ NPe nonionic surfactants under the commercial name of Tergitol were supplied by Dow Chemicals, Cary, NC, and used as received. The molecular weights, chemical specifications, and thermodynamic parameters of different Tergitol NPe surfactants ranging from NP7 to NP40 have been studied in detail, and documented by Dai and Tam.³² α - and β -cyclodextrins were purchased from Cerestar and used as received.

The prepared samples were placed in a water bath overnight at 40 °C to remove entrained air and subsequently left standing for 48 h prior to rheological measurements. All rheological experiments were performed at 25 °C in a TA Instruments AR-2000 stress-controlled rheometer using primarily a cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. As reported in the literature,³³ the steady shear response of HASE polymer/surfactant systems is sensitive to the shear history. To overcome this issue, 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 stress value that lied within the linear viscoelastic regime. This value was subsequently used in the dynamic frequency sweep test. All rheological experiments were run at least twice to ensure reproducibility.

UV/vis spectrophotometry measurements were performed on a JASCO V550 UV/vis spectrophotometer (JASCO Inc., Easton, MD). 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. The surfactant/cyclodextrin solutions were prepared in vials and kept in a constant-temperature water bath. The sample temperature was controlled using a digital stirring hot plate (Torrey Pines Scientific, San Marcos, CA) with the thermocouple inserted in the solution. Each measurement was conducted at least three times to ensure accuracy.

3. Results and Discussion

Addition of either α - or β -CDs substantially reduces the viscosity as well as viscoelastic properties of the HASE polymer. Previous work done by our group^{18,20} shows that the drop in the value of rheological properties asymptotes off at a CD concentration of 30 mol/mol of hydrophobic macromonomer irrespective of the type of CD. This concentration corresponds to 3.3 mM CD for the case of 0.5 wt % HASE, the polymer concentration used in this study. It is believed that CDs completely encapsulate the polymer hydrophobes at this concentration, thereby breaking all hydrophobic junctions present in solution. Since we intend to investigate the effect of surfactants on the recovery of rheological properties, we selected a 0.5 wt % HASE/3.3 mM CD as one of our two reference samples, the other being a 0.5 wt % HASE polymer-only solution.

Figure 2 compares the viscosity behavior of various surfactants on the 0.5 wt % HASE/3.3 mM α -CD solution. The molar ratio of surfactant to CD is kept constant at 3:1. As shown in the figure, addition of 3.3 mM CD to the base polymer causes a reduction in steady-state viscosity by almost 2 orders of magnitude. Upon addition of surfactants, contrasting behaviors are observed depending on the surfactant HLB. Compared to the original HASE solution, the viscosity is 2 orders of magnitude higher in the case of NP6, while no viscosity recovery is witnessed for solutions containing NP15. NP8, which has an intermediate

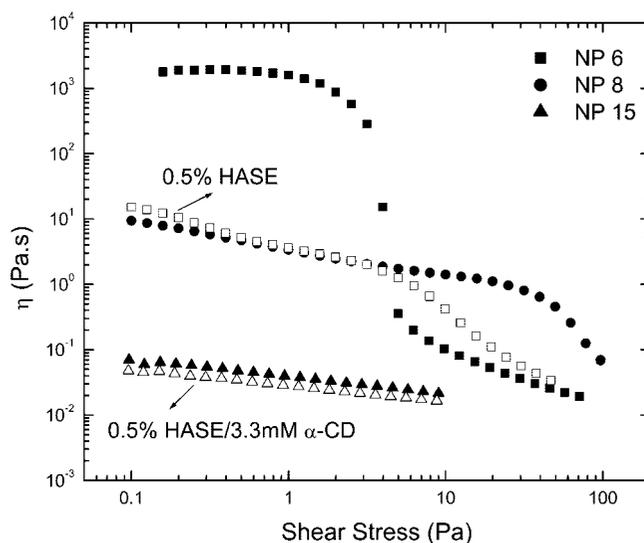


Figure 2. Effect of addition of various NP surfactants on the steady shear viscosity of a 0.5 wt % HASE solution containing 3.3 mM α -CD. The molar ratio of NP to α -CD is 3:1.

HLB between NP6 and NP15, exhibits a viscosity profile overlapping with the original HASE solution at low stresses. In the following sections, we probe further the observed dramatic differences by exploring the rheological behavior and clouding phenomena in HASE solutions containing either α - or β -CD at different concentrations of the above-mentioned surfactants.

3.1. Viscosity Modulation by Incorporating NP6 Surfactant.

Figure 3a shows the viscosity versus stress profile for 0.5 wt % HASE solutions containing α -CD in the presence of NP6 surfactant. NP6 is a low-HLB surfactant; its addition to pure HASE polymer solution is known to cause a continuous increase in low shear viscosity with increasing surfactant concentration, which is ascribed to the formation of large lamellar structures by surfactant molecules.^{15,33} A systematic addition of NP6 surfactant to this HASE/CD system leads to an increase in solution viscosity. At low concentrations of NP6, the solutions exhibit a viscosity profile mimicking that of the HASE/ α -CD system, a steady decline in viscosity with increasing stress. With a further increase in NP6 concentration, the viscosity profile becomes increasingly shear thinning at low stresses. The low shear viscosity of the original HASE solution without any CD is completely recovered at 5 mM NP6 concentration corresponding to 1.5 guest NP6 molecules per single host CD molecule. The association between the surfactant and CD is apparently strong enough to remove CDs from HASE polymer hydrophobes, thereby reactivating the hydrophobic junctions to form the transient network, as shown schematically in Figure 4b. Upon further increasing the NP6 concentration to 10 mM (or 3:1 NP6/ α -CD), the low shear viscosity becomes almost 2 orders of magnitude higher than that of the original HASE solution. The sample also exhibits a sharp drop in viscosity at a critical stress. The increase in viscosity over and above the original HASE viscosity can be attributed to interactions between NP6 and “free” polymer hydrophobes to form hydrophobic junctions incorporating both surfactant and polymer hydrophobes.^{15,34} A schematic representation of the molecular interactions in the HASE/CD system with increasing surfactant concentration is shown in Figure 4.

An interesting observation in Figure 3a is the relative magnitude of viscosity observed for the 1.5:1 NP6/ α -CD solution versus

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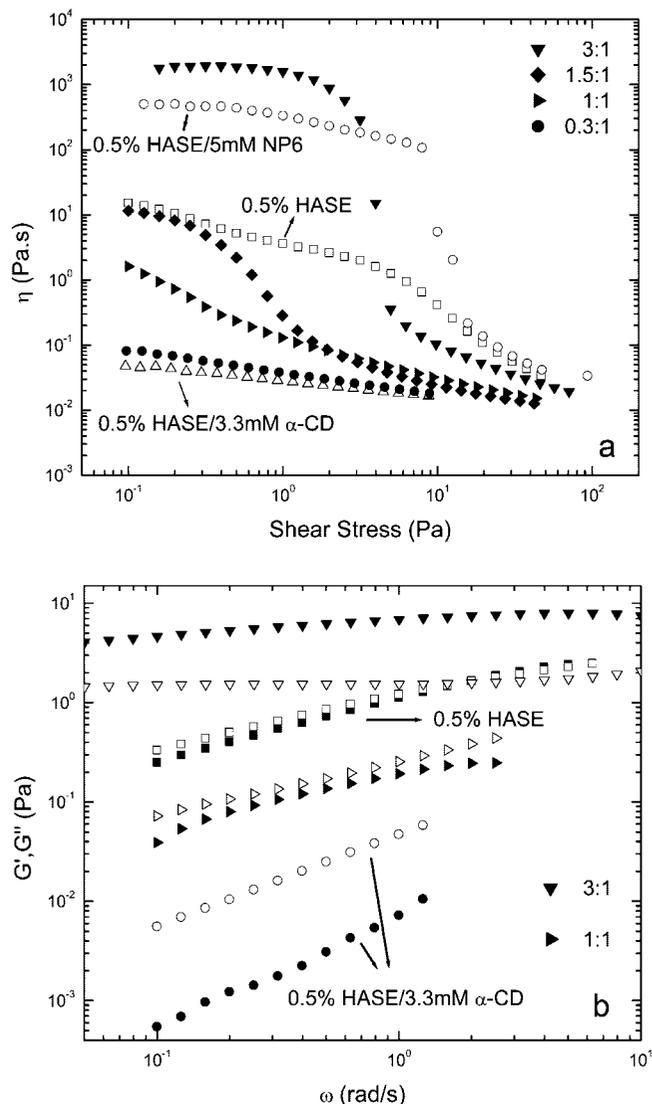


Figure 3. Effect of NP6 addition on the (a) steady shear viscosity and (b) dynamic moduli of a 0.5 wt % HASE solution containing 3.3 mM α -CD. The legends show the molar ratios of NP6 to β -CD. Closed symbols denote G' , and open symbols denote G'' .

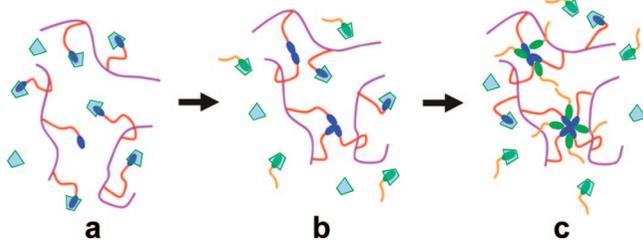


Figure 4. Schematic representation of the molecular interactions in the HASE/ α -CD system with increasing NP6 surfactant concentration: (a) HASE polymer molecules with hydrophobes encapsulated by CD, (b) recovery of hydrophobic junctions as surfactant addition facilitates removal of CDs from polymer hydrophobes and onto surfactant molecules, leading to regaining of the original HASE solution viscosity, and (c) surfactant molecules participating in hydrophobic junctions, resulting in viscosities over and above the original HASE viscosity.

that with the same amount of NP6 (5 mM) but with no CD (shown in the same figure). We find the viscosity of the CD-containing solution to be lower, suggesting that relatively fewer numbers of surfactants are able to participate in the hydrophobic

junctions, with the rest still forming complexes with the cyclodextrin.

Another notable feature observed in Figure 3a is the pronounced shear thinning observed for samples containing high NP6 concentration. In particular we notice a drastic drop in viscosity for the HASE/5 mM NP6 and the HASE/NP6/CD (3:1 molar ratio of NP6 to CD) samples at a critical stress. A similar behavior in viscosity has previously been observed in associative polymer/surfactant systems and attributed to the disruption of the associative network when the applied stress exceeds the overall strength of the hydrophobic junctions.^{35,36} For the HASE/NP6 solutions without CD, the critical stress is higher than that with CD, indicating a higher strength network. In the presence of CD, the concentration of active surfactant that can complex with hydrophobes decreases, resulting in a decrease in critical stress. It should be pointed out that the catastrophic viscosity reduction at a specific shear stress has also been ascribed to shear banding flow instabilities similar to that observed in wormlike micelles.^{10,14–16} We will not delve further into this feature observed in our system as this is a study in itself and beyond the scope and goals of this paper.

We attempt to derive additional information on the molecular interactions in solution by conducting dynamic rheological experiments on some selected systems. The dynamic frequency spectrum of 0.5 wt % HASE/ α -CD solutions in the presence of NP6 surfactants is shown in Figure 3b. The frequency spectrum of the 0.5 wt % HASE solution displays a viscous dominated response ($G'' > G'$) at low frequencies followed by an elastic dominated behavior ($G' > G''$) at higher frequencies. The inverse of the crossover frequency—the frequency at which G' equals G'' —gives the characteristic relaxation time of these systems, which is an estimate of the average strength of the mechanically active hydrophobic junctions in solution. Thus, with the formation and strengthening of a network, this crossover is expected to move to lower frequencies or longer time scales and vice versa. Moreover, transient network theory predicts that the elastic modulus at high frequencies is directly proportional to the number of mechanically active junctions.^{37,38} The addition of α -CD to the HASE solution served to reduce both elastic and loss moduli and increased their dependence on frequency as was observed earlier.¹⁸ These results imply an overall weaker network structure arising from a reduction in the number of active junctions in the HASE solution due to deactivation of the hydrophobic groups.

Upon the addition of NP6, both G' and G'' values trend upward, following the trends exhibited by the low shear viscosity of each sample. In addition, as the concentration of surfactant increases, the response becomes elastic dominated, with G' values surpassing those of G'' in the frequency range studied, and both the moduli exhibit a lower dependence on frequency. The crossover frequency, although not observed in the frequency range studied, appears to shift to lower values, indicating the strengthening of the polymer network. These results further support the notion that addition of NP6 removes CDs from polymer hydrophobes, thereby reactivating the original hydrophobic junctions and the resulting transient network. At the highest concentration of NP6 studied, the values of dynamic moduli exceed those of the original HASE solution with G' greater than G'' over the entire frequency range. This response is typical of gel-like behavior in the system and was witnessed earlier in certain associative polymer systems.³⁹

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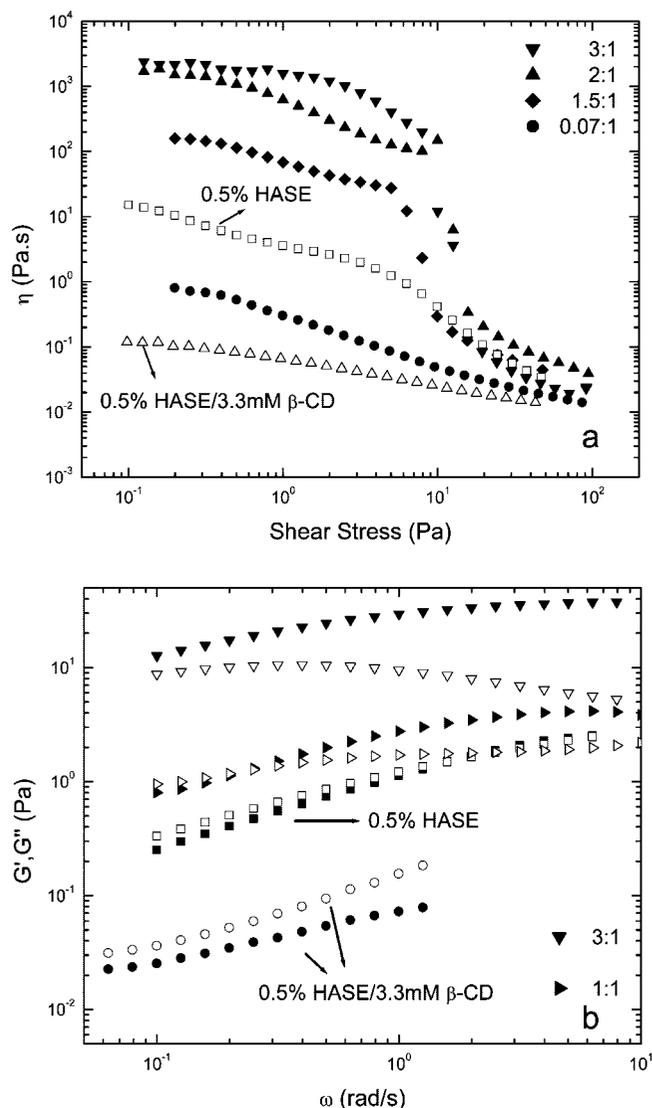


Figure 5. Effect of NP6 addition on the (a) steady shear viscosity and (b) dynamic moduli of a 0.5 wt % HASE solution containing 3.3 mM β -CD. The legends show the molar ratios of NP6 to β -CD. Closed symbols denote G' , and open symbols denote G'' .

The presence of a gel-like structure is further corroborated by the viscosity profile for the above polymer/surfactant/CD system (cf. Figure 3b) which displays a drastic drop in viscosity at a critical stress similar to the yield stress phenomena associated with physical gels.⁴⁰

Figure 5a shows the steady shear profile for 0.5 wt % HASE solutions containing β -CD in the presence of NP6 surfactant. We see that the extent of viscosity reduction of the original HASE solution is less in the case of β - as compared to α -CD. These results are consistent with observations made by Ma-hammad et al.^{18,20} for the same polymer/CD systems, albeit for higher HASE concentrations. As in the case of α -CD, adding NP6 to mixtures of HASE and β -CD greatly increases the solution viscosity, with high concentrations of NP6 leading to zero shear viscosities more than an order of magnitude greater than the original HASE solution. At low NP6 concentrations, viscosity profiles match that of an HASE/CD solution without any surfactant—low viscosity and uniform shear thinning without any sudden drop at higher stresses—while at higher concentrations,

considerably larger low shear viscosities are obtained that show a sudden drop at high stresses. However, an obvious difference in viscosity recovery between the two cases of α - and β -cyclodextrin lies in their rates upon NP6 addition. Whereas in the case of α -CD, low than viscosity recovery of the original solution is observed at an NP6 to CD ratio of 1.5:1, the same ratio in the case of β -cyclodextrin results in a viscosity over an order magnitude higher than that of the original HASE solution. This reflects a stronger affinity of β - versus α -cyclodextrin toward the hydrophobic nonylphenol group of the nonionic surfactant. The trends of dynamic moduli are consistent with those of the steady-state viscosity profile, and the moduli exhibit a stronger recovery when compared to the case of α -CD (Figure 5b). We verify this aspect subsequently in later sections by exploiting the clouding behavior of NP surfactants.

3.2. Role of the Surfactant HLB in Viscosity Modulation.

Since the HLB of a nonionic surfactant plays a significant role in determining both surfactant-CD and surfactant-polymer interactions, varying the nonionic surfactant HLB is expected to affect viscosity recovery in HASE solutions containing cyclodextrin. Thus far, we considered NP6 surfactant, which is a poorly water-soluble low-HLB surfactant. We now explore viscosity recovery from nonionic surfactants of the same homologous series but with longer hydrophilic parts (or higher HLB values). We select NP8 and NP15 surfactants having average EO chain lengths of 8 and 15, respectively. Similar to NP6, the addition of NP8 to mixtures of HASE and α -CD increases the viscosity of the solution with increasing concentration (Figure 6a). The recovery, however, is retarded in this case, reflecting a weaker affinity of NP8 to bind with α -CD. Moreover, unlike NP6, wherein the low shear viscosity is almost 2 orders of magnitude higher than the original solution viscosity at 10 mM concentration (3:1 NP8/ α -CD), the solution viscosity did not exceed the HASE viscosity at this ratio. The viscosity stabilized at values close to the original HASE solution, as both 10 mM NP8 with 3.3 mM α -CD and 19 mM NP8 with 2.2 mM α -CD (not shown for the sake of clarity) showed very similar viscosity profiles. An even more contrasting behavior to that of NP6 is observed in the case of NP15 surfactants (Figure 6b). A systematic addition of NP15 to the HASE/ α -CD solution reveals a minimal effect on either the low shear viscosity or its stress profile. While the viscosity does vary, these variations are small and do not provide a meaningful trend in the concentration range of NP15 studied. The unvarying viscosity of the HASE/CD solution in the presence of NP15 indicates the absence of any NP15-CD complexation or removal of α -CDs from polymer hydrophobes. Evidently, interactions between the polymer hydrophobe and surfactant are subdued in the case NP8 and minimal for NP15 as it would be reasonable to assume that, for those interactions to exist, polymer hydrophobes would first need to be “unmasked” of CDs and be free to interact with surfactant. These results indicate a stronger affinity of α -CD to bind with nonionic surfactants with a more hydrophobic character (lower HLB). The efficacy of viscosity recovery in HASE/ α -CD solutions appears to be strongly dependent on the hydrophilic chain length and in turn the HLB of the nonionic surfactant.

An entirely different trend of viscosity recovery is witnessed upon NP8 addition in the case of HASE solutions containing β -CD instead of α -CD as shown in Figure 7a. Low concentrations of NP8 dramatically increase the magnitude of low shear viscosity, while maintaining the steady shear thinning, and without a pronounced drop in viscosity at higher stresses. Instead of a monotonous increase as with α -CD, the viscosity exhibits a maximum at an NP8 concentration of 3.3 mM which corresponds

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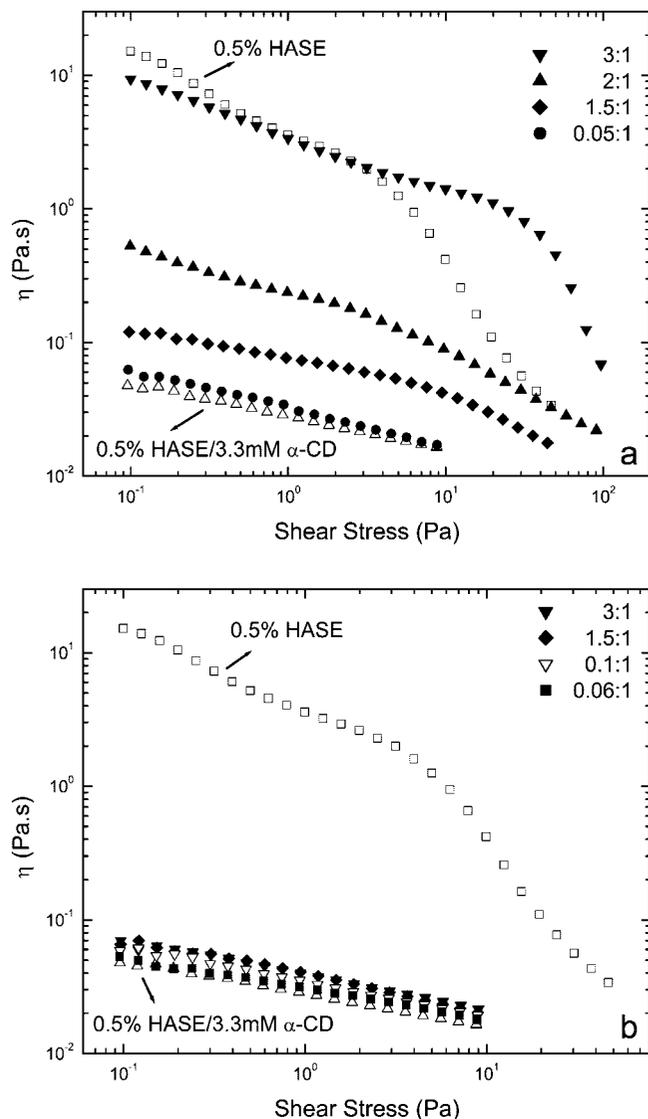


Figure 6. Effect of addition of (a) NP8 and (b) NP15 on the steady shear viscosity of a 0.5 wt % HASE solution containing 3.3 mM α -CD. The legends show the molar ratios of NP6 to α -CD.

to an NP8 to CD ratio of 1:1. The low shear viscosity at this concentration is almost a magnitude higher than that of the original HASE solution and shows a sudden drop in viscosity with shear stress, as seen earlier in the case of NP6. Increasing the surfactant concentration beyond this point lowers the viscosity of the solution from its maximum to around that of the original HASE solution at the maximum studied concentration. These observations can be explained in terms of negative interaction between NP8 and HASE polymer at higher surfactant concentrations. It was reported earlier that an increase in the NP8 concentration in a pure HASE polymer solution results in an increase in viscosity and viscoelastic properties of the HASE solution to a maximum followed by a decline to a value even lower than that of the solution viscosity. The rise in viscosity has been attributed to the formation of mixed micelles incorporating both polymer and surfactant hydrophobes, resulting in a stronger overall network, while the ensuing decrease in viscosity is the result of saturation of polymer hydrophobes by surfactant micelles at higher concentrations.^{15,34} These surfactant-saturated polymer hydrophobes are unable to participate in hydrophobic junctions, thereby weakening the overall network, which translates into a lower viscosity and gradual shear thinning as opposed to a sudden drop in viscosity.

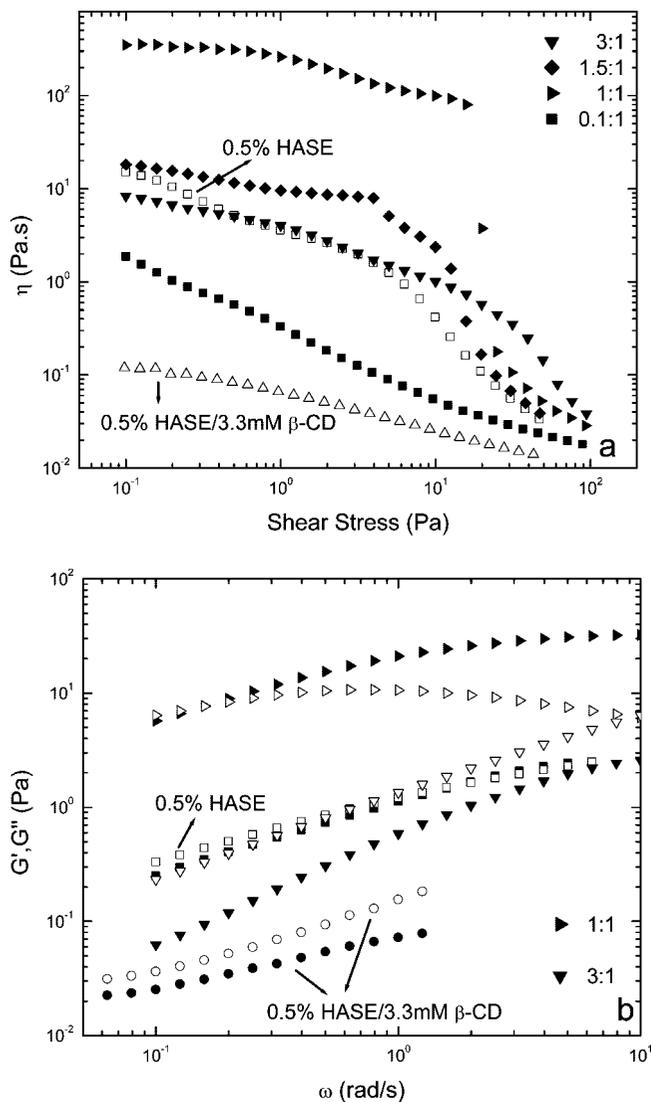


Figure 7. Effect of NP8 addition on the (a) steady shear viscosity and (b) dynamic moduli of a 0.5 wt % HASE solution containing 3.3 mM β -CD. The legends show the molar ratios of NP8 to β -CD. Closed symbols denote G' , and open symbols denote G'' .

Figure 8 shows a schematic representation of the surfactant-saturated polymer hydrophobes at high NP8 surfactant concentration, which results in a decrease in solution viscosity.

The frequency spectrum of the dynamic moduli for these systems (Figure 7b) further confirms the above hypothesis wherein addition of NP8 results in an initial increase in the moduli above that of the original HASE solution at a 1:1 NP8: β -CD ratio followed by lower values of the moduli at a surfactant to CD ratio of 3:1. Moreover, the dynamic moduli become less frequency dependent at first and then revert back to higher frequency dependence, reflecting formation and strengthening of a network structure upon NP8 addition and subsequent weakening at higher concentrations. Similar observations are made in the trend of viscosity recovery of a HASE solution containing β -CD in the presence of NP15 surfactant (Figure 9). A notable difference however is the maximum in viscosity achieved upon NP15 addition, which is greater than the HASE viscosity but significantly lower than that in the case of NP8. This is not completely unexpected as NP15 addition to a pure HASE solution does not result in an appreciable increase in viscosity.¹⁵

The above observations highlight the distinction in the complexation behavior of α - versus β -cyclodextrin with nonionic

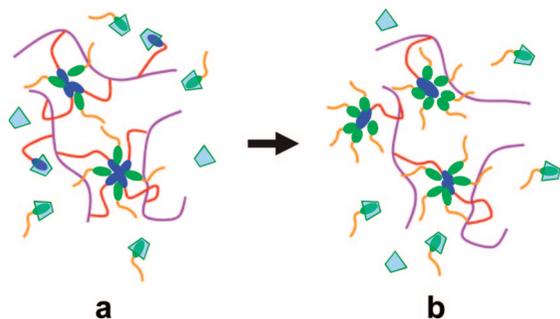


Figure 8. Schematic representation of the molecular interactions in the HASE/ β -CD system with increasing NP8 surfactant concentration: (a) surfactant molecules participating in hydrophobic junctions, resulting in viscosities over and above the original HASE viscosity and (b) formation of individually surfactant-saturated hydrophobic junctions, resulting in a disruption of hydrophobic junctions and leading to a decrease in viscosity.

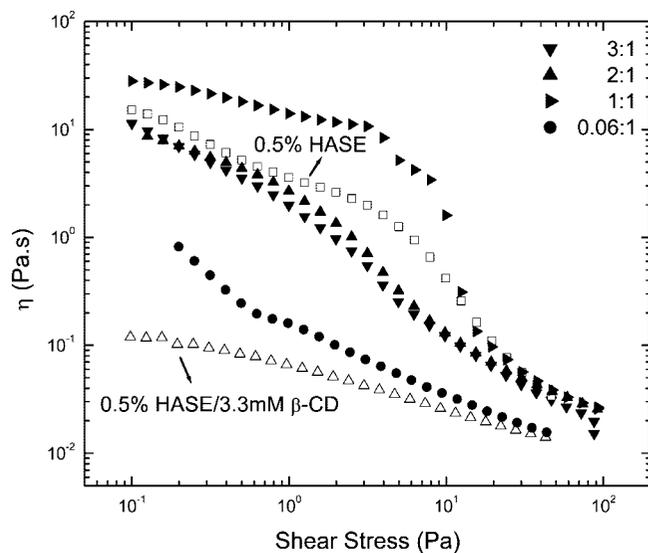


Figure 9. Effect of NP15 addition on the steady shear viscosity of a 0.5 wt % HASE solution containing 3.3 mM β -CD. The legend shows the molar ratios of NP6 to β -CD.

surfactants. In the case of α -CD, increasing the surfactant HLB diminishes the formation of surfactant/CD complexes, which results in either a retarded response (NP8) or absence (NP15) of viscosity recovery upon surfactant addition. On the other hand, in the case of β -CD, the surfactant-CD complexation is apparently not affected much by changing the surfactant HLB and the trends of viscosity appear to be dictated by interactions between the surfactant and polymer hydrophobes. Nonetheless, HLB values play a vital role in these systems as the surfactant-polymer interactions are, in turn, governed by the surfactant HLB as previously reported.⁴¹ To further understand the difference in the complexation behavior of α - versus β -cyclodextrin with nonionic surfactants, we investigate the clouding behavior of these surfactants in the presence of both α - and β -cyclodextrin as discussed in the next section.

3.3. Clouding Phenomena in NP Surfactants. A unique characteristic of oxyethylated nonionic surfactants is the display of clouding phenomena due to surfactant phase separation into micelle-rich and micelle-poor phases above a certain temperature. This behavior is explained in terms of formation of larger aggregates as well as stronger interaction between micelles owing to the dehydration of EO groups with increasing temperature.²⁸ The temperature at which the aqueous solutions become visibly turbid is termed the cloud point temperature (CPT). In general,

it has been observed that cloud point temperatures of poly(oxyethylene) surfactants increase with an increase in the number of EO units present in the molecule. For instance, above their cmc values, NP6 is cloudy at ambient temperatures, while the CPT of NP15 is greater than 100 °C. An interesting feature of CD-surfactant complexation is the introduction of a new equilibrium in the system that interferes with the self-assembly of surfactants into micelles or other aggregates,²⁶ which in turn influences their clouding phenomena. Martinez et al.⁴² studied the interaction of NP5 surfactant with β -cyclodextrin in terms of its clouding behavior. According to the authors, addition of β -cyclodextrin declouds the NP5 surfactant solution by binding with the hydrophobic group of the surfactant molecule. This surfactant-CD complexation disrupts the surfactant aggregates and inhibits phase separation. A cyclodextrin-induced shift in CPT was also observed by Na et al.⁴³ wherein addition of 2-(hydroxypropyl)- β -cyclodextrin effectively raised the CPTs of a variety of nonionic surfactants, especially those having a benzene ring.

To further our understanding of the nature of CD-surfactant interactions in α - and β -cyclodextrin, we performed a series of cloud point experiments on CD/surfactant mixtures. As aforementioned, NP6 surfactants are insoluble in aqueous solutions and hence cloudy at room temperature at concentrations above their cmc and have a CPT less than 0 °C. Figure 10 shows images of a 1 mM NP6 solution by itself as well as in the presence of α - and β -cyclodextrin. As can be seen in the figure, a laser beam projected through the NP6 solution shows scattering in the solution, presumably due to presence of aggregates. Upon the addition of cyclodextrin to the surfactant solution, the NP6:CD molar ratio being 1:2, no scattering is visible in the presence of β -cyclodextrin, while scattering of the laser beam persists in solutions containing α -cyclodextrin. These observations clearly reflect a stronger affinity of NP6 to β -cyclodextrin as compared to α -cyclodextrin. β -Cyclodextrin encapsulates the hydrophobic group of surfactant, causing a disruption of aggregates and hence declouding. On the other hand, the existence of scattering in the case of α -cyclodextrin implies partial or no disruption of the micellar aggregates, signifying a weaker binding of NP6 with α -cyclodextrin.

We followed up these qualitative measurements with quantitative UV/vis spectroscopy measurements on solutions with NP6:CD ratios of 1:1 and 1:2 (Figure 11). As is evident from the transmittance curves in the visible spectrum, addition of β -cyclodextrin to the NP6 solution increases its transmittance significantly, which approaches 100% at a 1:2 NP6:CD ratio, confirming the housing of the NP6 hydrophobe within the cavity of β -cyclodextrin. In contrast to β -cyclodextrin, the transmittance curve of NP6 solutions containing α -cyclodextrin is slightly lower than that of a pure NP6 solution at a 1:1 NP6:CD ratio. The transmittance (%) increases on further addition of α -CD, but the values are considerably lower than those in the presence of β -CD. These results further confirm a stronger affinity of binding of NP6 with β -CD. This dependence of the degree of binding with surfactants on the type of CD is generally explained in terms of the difference in their cavity diameters (~ 5.2 Å for α -CD and ~ 6.6 Å for β -CD), which affects the snugness of the fit between the host and the guest molecule.^{20,21,26,44} As a next step, we measured the transmittance in NP6/CD solutions in the presence

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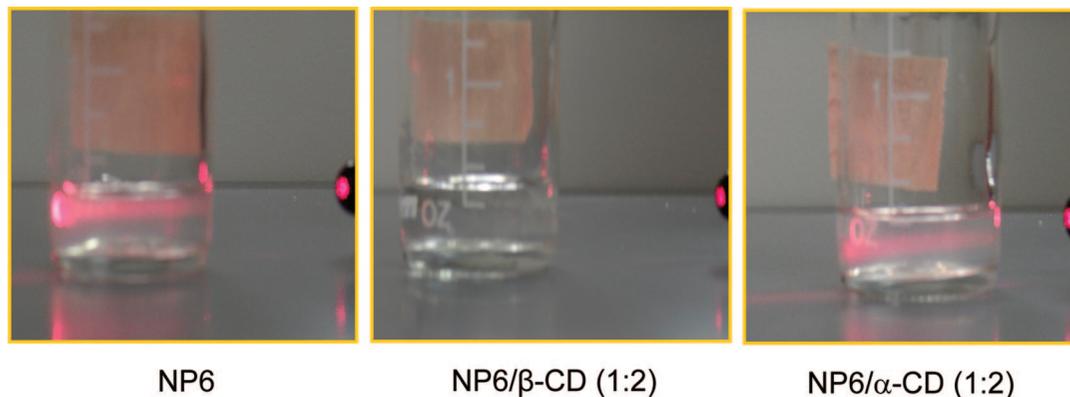


Figure 10. Scattering of a laser beam in 1 mM NP6 solution with and without the presence of α - and β -cyclodextrin in a 1:2 molar ratio. Scattering disappears in the presence of β -cyclodextrin, while it is still present in the case of α -cyclodextrin.

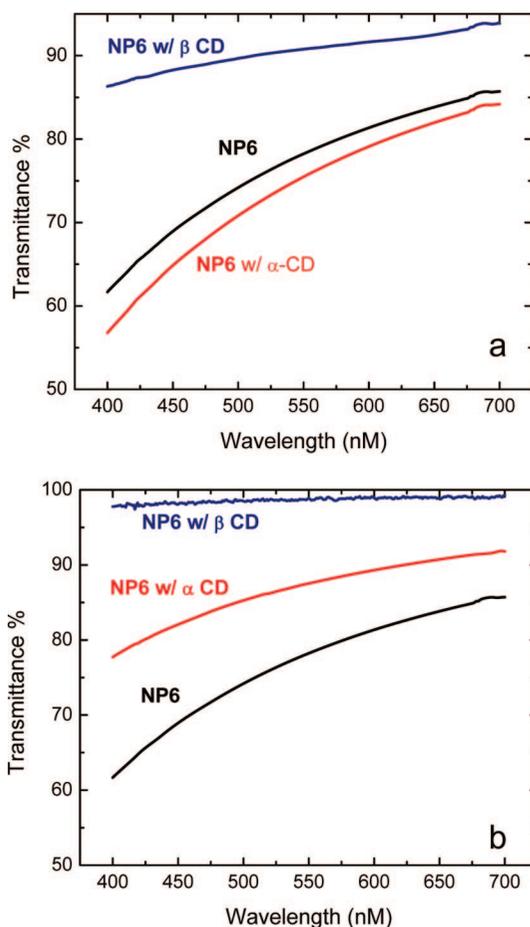


Figure 11. UV/vis spectrum of a 1 mM NP6 solution with α - and β -cyclodextrin in NP6:CD ratios of (a) 1:1 and (b) 1:2.

of 0.5 wt % HASE (Figure 12). The CD concentration was fixed at 3.3 mM as used in the rheological studies. HASE solutions show similar high transmittance values in the presence of either α - or β -CD. As NP6 is added to these solutions in a 1:2 NP6:CD molar ratio, the transmittance decreases in both the cases. Here again we find a much higher transmittance in the case of β - versus α -CD upon NP6 addition. A higher transmittance corresponds to a smaller number of NP6 molecules present as self-aggregates and hence less cloudiness. This in turn implies more NP6 surfactants are complexed with β -CD, suggesting a stronger binding affinity.

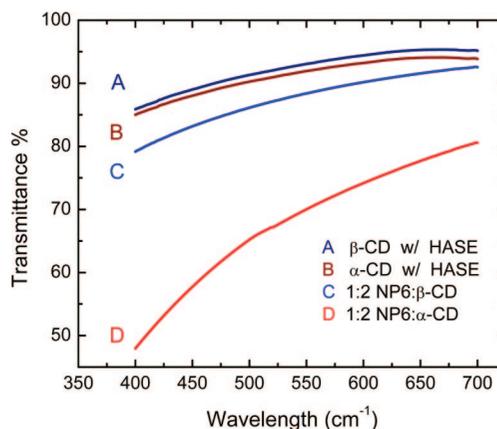


Figure 12. UV/vis spectrum of 0.5 wt % HASE/3.3 mM CD in the presence of NP6.

In the case of soluble surfactants such as NP8 that are not cloudy at room temperature, we measured the CPTs of surfactant solutions with and without CD. Addition of β -CD to a 5 mM solution of NP8 in a 1:2 NP:CD ratio raised its CPT from 50 to 79 °C. On the other hand, addition of α -CD causes a minor reduction of the CPT to 46 °C. These findings indicate that while β -CD delays the formation of micellar aggregates by encapsulating the surfactant hydrophobic groups, the interactions of α -CD with the surfactant hydrophobic group are not strong enough to be reflected in an appreciable change in the CPT. These differences in the binding affinities of CDs are reflected in the extent and the rate of viscosity recovery of HASE solutions using surfactants.

4. Conclusion

The modulation of hydrophobic interactions in HASE solutions in the presence of cyclodextrin is strongly affected by both the type of cyclodextrin and the HLB of the nonionic surfactant. Entirely different trends of viscosity as well as dynamic moduli are observed in the case of low-water-soluble surfactant (NP6) as compared to highly soluble surfactants (e.g., NP15). Raising the surfactant HLB in the case of HASE/ α -CD solutions shows a transition from a monotonous increase in low shear viscosity in the case of NP6 to an absence of viscosity recovery in the case of NP15. On the other hand, HASE/ β -CD mixtures exhibit complete recovery and further viscosity enhancement upon addition of the surfactants studied. However, unlike that of NP6, addition of NP8 and NP15 leads

to a lowering of the viscosity at higher concentrations after a maximum is attained. These results are explained in terms of a stronger binding affinity of nonionic surfactants for β - versus α -CD as confirmed by UV/vis spectroscopy and cloud point measurements. Moreover, the binding affinity decreases with increasing surfactant HLB especially in the case of α -CD. The interaction of surfactant molecules with the polymer hydrophobes, as governed by the surfactant HLB, plays a dominant role in determining the eventual viscosity values

once the original HASE viscosity is recovered. These results imply that the surfactant HLB is a key factor to be considered while employing surfactants to facilitate rheological modification in HASE solutions containing cyclodextrin.

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