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Effects of nonionic surfactant on the rheological property of associative polymers in complex formulations

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Abstract

The rheological properties of hydrophobically modified ethoxylated urethane (HEUR) were investigated in the presence of a nonionic surfactant, polyoxyethylene stearyl ether ($C_{18}(EO)_{20}$). The presence of nonionic surfactants played an important role in tuning the rheological properties of HEUR aqueous solutions. Observing both plateau modulus and viscoelastic relaxation time of HEUR aqueous solutions with varying the concentration of $C_{18}(EO)_{20}$ allowed us to demonstrate that $C_{18}(EO)_{20}$ readily interacts with the hydrophobic segments of HEUR polymers, which eventually formed a strong micellar network. Moreover, the micellar network formed at a critical concentration of $C_{18}(EO)_{20}$, ~0.6% w/v, was indeed stable against both ionic strength and pH in the aqueous medium and complex formulations, such as a colloid suspension and an oil-in-water emulsion, thus providing more practical applications as thickeners for a wide variety of complex formulations.

Keywords: Hydrophobically modified ethoxylated urethane (HEUR); Nonionic surfactants; Rheological properties

1. Introduction

Thickeners are water-soluble polymers that are able to expand their chains by absorbing large amount of water, accompanying an increase of viscosity in solution. This viscosity behavior of thickening polymers in water makes them desirable for a wide variety of industrial applications, including coatings [1–3], foods [4–6], bio-formulations [7–9], and cosmetics [10,11]. The formulations for those applications may contain various types of ingredients for giving specific functions to the final products. However, such formulation processes result in a drastic change in the viscosity by changing the pH or ionic strength of the medium, or by inducing specific interactions with suspending materials. This is an undesirable side effect since the degree of thickening is essential for the stability in given complex formulations.

One method of overcoming this limitation is to use the associative polymers [12–17], hydrophobically modified water-soluble polymers, in the complex formulations. A well-known associative polymer is a hydrophobically modified ethoxylated urethane (HEUR) that consists of a poly(ethylene oxide) (PEO) backbone chain-extended by diisocyanates and two long hydrophobic alkyl chains on both ends [16–21]. Typically, they associate through hydrophobic interactions in aqueous solutions, depending on the concentration and molecular structure. They produce different types of micelles or aggregates, which are essentially related with their solution behaviors in aqueous phases, thus changing the rheological properties [22–24]. One of the promising properties that make them useful as a thickener is that as the concentration

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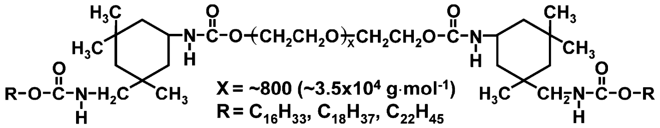
increases, the hydrophobic segments of HEUR polymers bridge the micelles into a limitless network in aqueous solutions, resulting in a sharp increase in the viscosity.

To further expand their applicability, there have been efforts to understand the effect of surfactants on their viscosity behaviors [25–27]; for example, by adding an appropriate amount of sodium dodecyl sulfate (SDS) to HEUR solutions, the higher viscosity can be obtained because hydrophobic stickers replaced by SDS molecules give rise to a larger number of bridging junctions. The presence of surfactants in HEUR solutions is critical in controlling the viscosity and providing the additional desirable stabilities. However, in many applications, such as foods, pharmaceuticals, and cosmetics, the use of most common ionic surfactants is strongly restricted due to the safety issue [28–30]; it is required to use the safe nonionic surfactants. From the standpoint of thickening performance and safety, there is a need for a thickening system that can control the viscosity irrespective of the type of formulations and allow us to solve the safety issues in the ultimate applications.

In this communication, we tried to understand the rheological properties of HEUR aqueous solutions in the presence of nonionic surfactants, which allowed us to obtain a robust means to control the rheological properties of a wide variety of complex formulations. We used polyoxyethylene stearyl ether, $C_{18}(EO)_{20}$, as a model nonionic surfactant that has been widely used in pharmaceuticals and cosmetics. This thickening system provides both stability and safety to the formulations. In this study, we observed the effect of $C_{18}(EO)_{20}$ on changing the viscosity of HEUR aqueous solutions. Furthermore, we prepared a couple of complex formulations, a silica suspension and an oil-in-water emulsion, stabilized by HEUR and $C_{18}(EO)_{20}$, and showed their viscosity behaviors against the change of ionic strength and pH to experimentally confirm the applicability as practical thickeners.

2. Experimental methods

We synthesized HEURs by using a stepwise urethane reaction [31,32]. First, we prepared a urethane prepolymer consisted of a POE in the middle and two isocyante groups on both ends by stoichiometrically reacting 1 mol of POE ($M_n \sim 3.5 \times 10^4$ g mol^{-1}, Fluka) with an excess of isophorone diisocyanate (1:20 equivalent ratio, IPDI, Aldrich). This reaction was carried out in a 1 L four-necked glass flask, equipped with a Dean–Stark water trap, a condenser, a nitrogen inlet, and a mechanical stirrer. To completely remove the moisture that may exist in PEO and toluene, we used an azeotropic distillation process in the reactor: PEO (70 g) dissolved in toluene (400 mL) was completely dried by repeatedly removing four Dean–Stark water traps filled with toluene. After cooling the PEO solution to 45 °C, we dissolved a small amount of reaction catalyst, dibutyltin dilaurate (0.3 g, Aldrich). Continuously, by adding a stoichiometric amount of IPDI (8.9 g) to the PEO solution, a urethane reaction was carried out for 3 h at 45 °C. Then, two isocyanates end-capping the PEO prepolymer were reacted again with alkyl alcohols for 3 h at the same temperature. In this study, we used three different alkyl alcohols: 1-hexadecanol, 1-octadecanol, and 1-docosanol. The HEURs synthesized in toluene were precipitated in petroleum ether and recovered by collecting them on a sintered glass funnel. Finally, we dried the filtered HEURs under vacuum for 24 h. The molecular structure of HEURs synthesized in this study is shown in Scheme 1. Depending on the number of carbons in alkyl chains, we named them HEUR-C_{16}, HEUR-C_{18}, and HEUR-C_{22}.



Scheme 1. Molecular structure of HEURs.

The synthesized HEURs were dissolved in water that was distilled and deionized through a Millipore Q ion exchange and filtration. When observing the effect of nonionic surfactants, we added polyoxyethylene stearyl ether ($C_{18}(EO)_{20}$, Nihon Emulsion) to the HEUR solutions. We also prepared two representative complex formulations: a particle suspension and an oil-in-water (O/W) emulsion. A particle suspension was prepared by simply dispersing silica particles (3% w/v, ~3 μm Silos 3 M) with 2% w/v HEUR-C_{22} and 0.6% w/v $C_{18}(EO)_{20}$. We also prepared a simple O/W emulsion by homogenizing a 12 wt% oil mixture in water at 7.0×10^3 rpm for 5 min at 70 °C. The oil mixture consisted of polyoxyethylene sorbitan monostearate (Tween 60, 4% w/v), sorbitan stearate (Arlacel 60, 4% w/v), arachidyl behenyl alcohol/arachidyl glucoside (Montanov 202, 8% w/v), silicone oil (DC 345, 40% w/v), and liquid paraffin (44% w/v). Then, the viscosity of the emulsion was adjusted to $\sim 2.3 \times 10^4$ Pa s. In this case of preparing emulsion samples, we could obtain a high viscosity with only 0.5% w/v HEUR-C_{22}, which seemed to be due to some interactions between HEUR and oils or additives, such as alkyl alcohols and other surfactants. The samples were prepared by adjusting the pH value by the addition of the necessary amounts of HCl or NaOH.

The rheological properties of these 2.0% w/v HEUR in aqueous solutions and complex formulations were measured with a TA rheometer (AR2000) at room temperature. Due to the high viscosity of the given samples, we measured a static viscosity in an oscillatory shear mode by using cone and plate geometries (1° angle and 4 cm diameter). In these measurements, a step-strain experiment allowed us to obtain a linear viscosity [33]: first, we determined a stress relaxation function, $G(t)$, by applying a deformation, γ_0, to the given sample and by detecting a stress, $\sigma(t)$, with the measurement of time. Here, we controlled deformation amplitudes from 1 to 30%. Then, we obtained $G(t)$ by following a formula: $G(t) = \sigma(t)/\gamma_0$.

3. Results and discussion

The rheological behavior of HEURs in aqueous solutions has been understood in terms of a transient micellar network formed by linking their micelles. Typically, hydrophobic free end tails of HEUR polymers transiently are associated with their micelles [18–21], which can be characterized by using a single particular relaxation time, as shown in Fig. 1; when the shear rate exceeds the inverse of the characteristic relaxation time, the micellar network created by hydrophobic interactions readily breaks down, resulting in a shear thinning. Moreover, the onset of shear thinning shifts to a lower shear rate with the increase in the length of alkyl chains, meaning that the relaxation time is proportional to the relative hydrophobicity of HEUR polymers. A stress relaxation function, $G(t)$, can be measured by step-strain experiments, as can be seen in Fig. 2. We observed that HEURs synthesized with varying the length of alkyl chains have fairly short time to which $G(t)$ remains constant; HEUR-C_{16} ~ 0.1 s, HEUR-C_{18} ~ 0.5 s, and HEUR-C_{22} ~ 10 s.

To better elucidate the underlying rheological property of HEURs in water, in this study, we modified the Maxwell model and obtained a more flexible approximation of $G(t)$ [33]:

$$G(t) = G_0 \exp[-(t/\tau)^{\alpha}] \qquad (1)$$

α was varied from 0 to 1 depending on the relaxation behaviors. The solid line through the data points in Fig. 2 proceeds from best fit calculations according to Eq. (1). The agreement is excellent. By using this, we could obtain an elastic plateau modulus, G_0, a relaxation time, τ and α. The G_0 was closely related to the number density of elastically active chains [34,35], ν_0, which can be illustrated by $G_0 = \nu_0 \kappa_B T$; τ corresponds to the lifetime of micelle junctions. We observed that as the length of alkyl chains increases from C_{16} to C_{22}, G_0 increased from ~250 to ~320 Pa, τ increased from ~0.1 to ~55 s, and α decreased from 0.93 to 0.84. The τ primarily depended on the length of hydrophobic chains. Thus, this result demonstrates that longer hydrophobic alkyl chains more strongly bridge HEUR micelles by increasing their hydrophobicity [19].

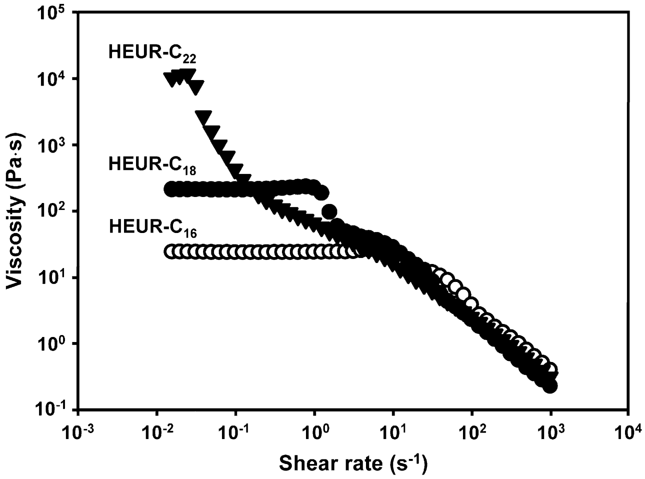


Fig. 1. Steady viscosity of HEUR aqueous solutions as a function of shear rate: HEUR-C_{16} (○), HEUR-C_{18} (●), and HEUR-C_{22} (▼). The concentration of HEURs was 2% w/v in water throughout the measurements.

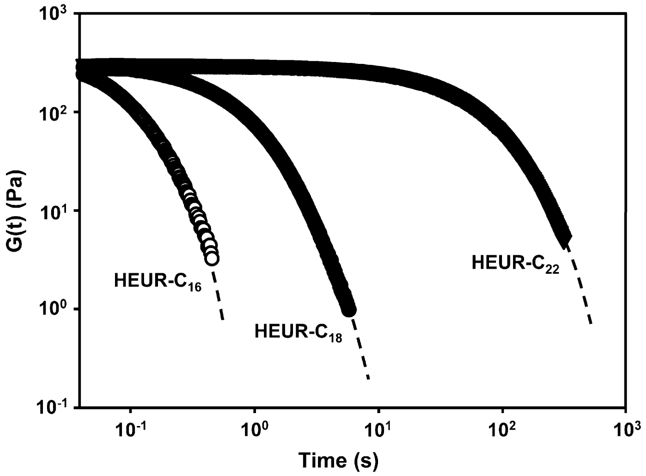


Fig. 2. Time dependence of stress relaxation functions, $G(t)$ of HEUR aqueous solutions in step-strain experiments: HEUR-C_{16} (○), HEUR-C_{18} (●), and HEUR-C_{22} (▼). The concentration of HEURs was 2% w/v in water throughout the measurements. The continuous lines are best fit calculations using a stretched exponential decrease (Eq. (1)).

Using the insights gained from studying the solution property of HEURs with different hydrophobicities, we were able to figure out the effect of a nonionic surfactant, $C_{18}(EO)_{20}$, on their low shear viscosity. The results are shown in Fig. 3. Adding surfactants usually provided HEUR micelles with more favorable hydrophobic associations in aqueous solutions, thus increasing the viscosity to a critical surfactant concentration. In case of using $C_{18}(EO)_{20}$, we also observed a similar trend: until reaching 0.6% w/v, the viscosity of the solutions gradually increased, which means that $C_{18}(EO)_{20}$ substitutes some of the HEUR end groups in the cores of the micelles and induces to form bridges between the micelles; a further increase in the concentration of $C_{18}(EO)_{20}$ saturates the cores and collapses the micellar structure, thereby lowering the solution viscosity (see the inset of Fig. 3). This result could be verified again by observing G_0 and τ of HEUR solutions with the concentration of $C_{18}(EO)_{20}$:HEUR solutions at ~0.6% w/v $C_{18}(EO)_{20}$ showed higher G_0 and τ by approximately 1.5 times by comparison to those of pure HEUR solutions. This confirms that $C_{18}(EO)_{20}$ readily interacts with the hydrophobes of HEURs, which eventually creates a physically strong micellar network at a critical concentration. Moreover, by changing the length of alkyl chains of HEURs from C_{16} to C_{22}, we were able to control their solution viscosity by the difference of three orders of magnitude, offering more flexible controllability of solution properties in the presence of nonionic surfactants.

An important feature of this thickening system consisted of HEUR and $C_{18}(EO)_{20}$ is that it provides a truly stable physical network in water. Using this unique advantage enabled us to maintain the solution viscosity even at various medium properties, such as the ionic strength and pH, as shown in Figs. 4 and 5. We attribute this to the fact that HEUR solution is thickened by the hydrophobic interaction between HEUR and $C_{18}(EO)_{20}$ and is independent of electrostatic forces. This

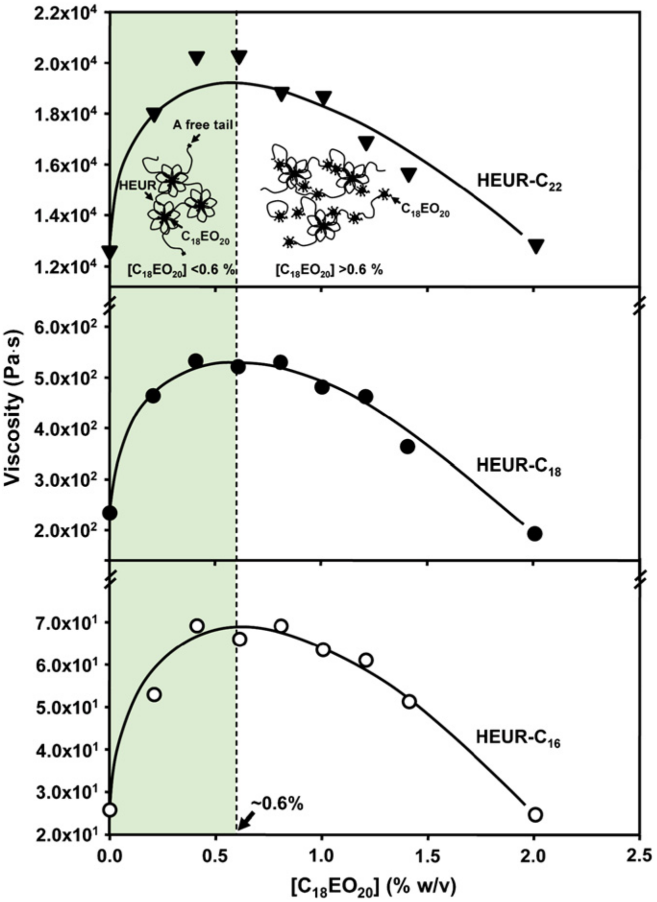


Fig. 3. Viscosity change of HEUR aqueous solutions with varying the concentration of polyoxyethylene stearyl ether, $C_{18}(EO)_{20}$: HEUR-C_{16} (○), HEUR-C_{18} (●), and HEUR-C_{22} (▼). Viscosity was measured at a shear rate, 0.02 s^{-1}. The concentration of HEURs in water was 2% w/v throughout the measurements. The inset shows the schematic microstructures of HEUR polymers before and after the saturation of their micelles by $C_{18}(EO)_{20}$.

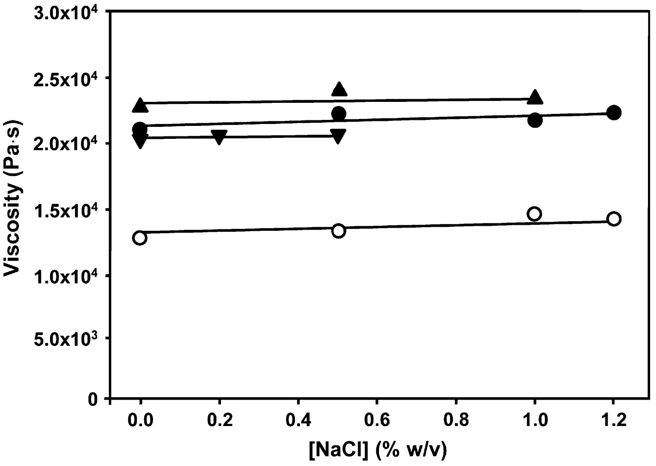


Fig. 4. Viscosity change of HEUR-C_{22} aqueous solutions (2% w/v) with varying ionic strength in the presence (●) and absence (○) of $C_{18}(EO)_{20}$. The effect of solid particles on the viscosity was observed by using a 3% w/v silica suspension (▼) prepared with 2% w/v HEUR-C_{22} and 0.6% w/v $C_{18}(EO)_{20}$. The effect of the oil drops stabilized by surfactants on the viscosity was also observed by using an O/W emulsion (▲) prepared with 0.5% w/v HEUR-C_{22} and 0.15% w/v $C_{18}(EO)_{20}$. Viscosity was measured at a shear rate, 0.02 s^{-1}.

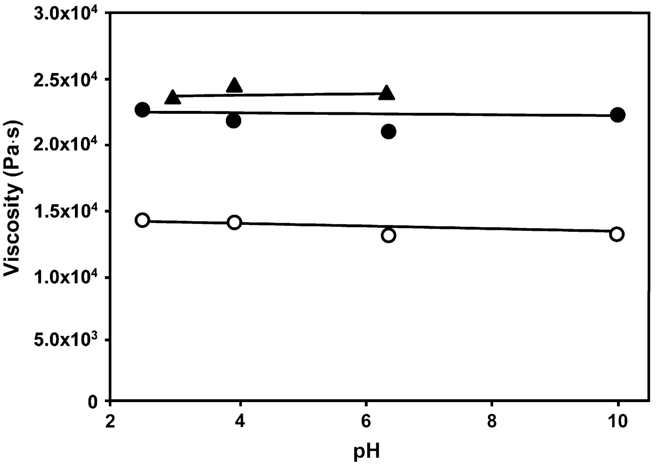


Fig. 5. Viscosity change of HEUR-C_{22} aqueous solutions (2% w/v) with varying pH in the presence (●) and absence (○) of $C_{18}(EO)_{20}$. The effect of the oil drops stabilized by surfactants on the viscosity was also observed by using an O/W emulsion (▲) prepared with 0.5% w/v HEUR-C_{22} and 0.15% w/v $C_{18}(EO)_{20}$. Viscosity was measured at a shear rate, 0.02 s^{-1}.

result is indeed inspiring because there have been some limitations in stabilizing the formulations that may contain a wide variety of additives. A more practical comparison of this thickening effect was possible by adding HEUR-C_{22} (2% w/v) and $C_{18}(EO)_{20}$ (0.6% w/v) into the complex formulations. In this study, we prepared two complex formulations, a silica suspension and an O/W emulsion, and measured their viscosity change with the ionic strength and pH. The results are shown in Figs. 4 and 5. The measured viscosities of these complex formulations were different from those of neat HEUR aqueous solutions. In the case of using the emulsion, we could obtain a high viscosity with a smaller amount of HEUR (~0.5% w/v). This appeared that there were some interactions between the micellar networks and silica particles or oil drops. Surprisingly, however, one common observation was that irrespective of the formulations, their viscosity remained constant against the change of the ionic strength and pH. This result experimentally conformed well that the micelle network solely formed by the interaction between the HEUR and nonionic surfactants was truly stable and could effectively stabilize a variety of formulations even in tough solution environments.

4. Conclusions

In this study, we tried to show the rheological properties of HEUR aqueous solutions in the presence of a nonionic surfactant, $C_{18}(EO)_{20}$. We have demonstrated that $C_{18}(EO)_{20}$ had importance and played a role in inducing a hydrophobic interaction with HEUR polymers and in providing more flexible control of their solution viscosity. At a critical concentration of $C_{18}(EO)_{20}$ that was approximately 0.6% w/v in this study, we could obtain the highest viscosity for given HEUR solutions, meaning a physically well connected micellar network had been formed. The formation of such a promising micellar network highlights the versatility of this thickening system; a wide variety of complex formulations with different types of ingredients can be freely produced without the sacrifice of their viscosity, which is critical in maintaining their original activity or performance.

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