Effect of nonionic surfactants on the electrorheology of emulsions

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Abstract

In this study, we consider the effect of nonionic surfactants on the rheological responses of emulsion systems under the action of a uniform dc electric field. The model emulsions consist of a less conducting dispersed phase and a more conducting continuous phase. When the shear flow is weak, the positive viscosity effect is produced due to the formation of chain-like morphology. The nonionic surfactants used here generate two distinctively different effects. Specifically, first, the steric hindrance induced by the surfactant molecules renders the structure unstable, and thereby reduces the degree of positive viscosity effect. Secondly, the presence of surfactant molecules also prevents the rotation of the dispersed droplets by anchoring across the interface or by decreasing the size of dispersed phase. The second effect suppresses the negative viscosity effect.

Key words : electrorheology, emulsion, surfactant effect

1. Introduction

A number of solid particle suspensions activated by the external field such as electric or magnetic field are known as electro-magneto responsive fluids [Rosensweig (1985), Block and Kelly (1988), Zukoski (1993)]. The electrorheological (or magnetorheological) responses describe the rapid but reversible change in the rheology of concentrated suspensions of fine particles in insulating liquids for the inception of a strong external electric (or magnetic) field. Electrorheological (ER) or magnetorheological (MR) fluids have been considered as an ideal interface between mechanical devices and electronic controls because rheological changes in the suspension occur in a very short time scale and with low power consumption. Ordinarily, the viscosity of ER or MR fluids is largely enhanced by applying an external electric or magnetic field due to the formation of chain-like morphology extended between the electrodes. If one attempts to slide one electrode relative to the other, the particle chains resist the deformation.

While the viscosity enhancement (the positive viscosity effect) of the suspension under the external field has been extensively studied, the extraordinary "negative viscosity effect" is often observed under certain conditions. Wu and Conrad (1997) studied the ER effect of a Teflon/silicone oil suspension with a dc electric field and observed the negative viscosity effect. They revealed that, under a dc

electric field, the Teflon particles migrated to the positive electrode resulting in a structure, which consisted of two layers; namely, a relatively pure liquid and a more concentrated suspension. The particle migration led to a decrease in the shear stress, producing the negative ER response. More rigorous theoretical and experimental results are available in the case of MR fluids [Shliomis and Morozov (1994), Bacri et al. (1995), Rosensweig (1996), Zeuner et al. (1998)]. A constant magnetic field balances the fluid vorticity and impedes the rotation of an individual magnetic particle. Thus, the magnetic energy is partially transformed into the angular momentum of the particles, which is in turn transferred into a hydrodynamic motion of the fluid. It manifests itself in a decrease of the total viscosity.

Recently, emulsion systems or equivalently immiscible liquid blends have attracted a great attention as a new generic type of ER fluids and its rheological responses in an electric field have been investigated [Tajiri et al. (1997, 1998, 1999), Pan and McKinley (1997), Kimura et al. (1998), Orihara et al. (1999), Ha and Yang (1999)]. In emulsion systems, both the positive and negative viscosity effects have been observed. Conceptually, when the dispersed phase is more conducting, the positive viscosity effect is produced, whereas the negative viscosity effect can be generated for the phase-reversed emulsions. It is obvious that the positive viscosity effect arises from the columnar morphology extended between two electrodes. The elongation of an individual droplet parallel to the direction of

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electric field is mainly responsible for the formation of liquid columns or bridges, while the continuous breakup and reformation of liquid columns proceed. On the other hand, the mechanism of negative viscosity effect is still not clear. Our research group has been studying the rheological behavior of oil-in-oil emulsions consisted of a less conducting dispersed phase and a more conducting continuous phase and observed the apparent negative viscosity effect for the first time in such emulsion systems [Ha and Yang (1999)]. Previously, we concluded that the electric-field-induced rotation of dispersed droplets is probably responsible for the negative viscosity effect, which is analogous to the MR fluids mentioned earlier. Fluid segregation into two adjacent phases of high and low volume fractions has been also observed in emulsion systems and may be another cause to the negative viscosity effect. However, the fluid segregation did not always accompany the viscosity reduction of emulsion systems in an electric field. According to Tajiri et al. (1999), the fluid segregation caused to the second mode slow transient responses following the first (faster) one.

In this study, the effect of nonionic surfactant molecules resided in the drop interface on the rheological responses is considered. The presence of surfactant molecules may produce a lot of complicated effects on the rheological behavior of emulsions [Pal and Rhodes (1989), Pal (1992)]. Due to the lowered interfacial tension, the size of dispersed phase can be reduced. In addition, if the surfactant concentration on the interface is nonuniform, the Marangoni flow can be generated [Ha and Yang (1995, 1999), Powar and Stebe (1996), Li and Pozrikidis (1997)]. By steric hindrance induced by the surfactant molecules, coalescence of the dispersed phase can be considerably inhibited. Of course, all of the aforementioned effects arising from the surfactant molecules have to be fully understood in

order to describe the rheological responses of emulsion systems more faithfully. However, in the present study, we restrict our attention to the effect of surfactant molecules on the electrorotation of the dispersed phase, which results in the negative viscosity effect in emulsion systems. It is anticipated that the presence of surfactant molecules between the drop and continuous phases may cause a distinctively different response in rheological behavior by altering the rotational motion of the dispersed droplets. The surfactant molecules have an amphiphilic structure, and therefore, anchor the dispersed and continuous phase. Consequently, the rotation of the droplets induced by reverse dipole and the vorticity of the ambient flow may be suppressed. Measuring the rheological response of emulsions reveals this effect.

2. Experimental

Model emulsions, consisting of silicone oil (KF-96, Shinetsu silicone Korea) drops dispersed in castor oil (Aldrich Chemical), were prepared by vigorous mechanical agitation. The volume fraction of dispersed phase was fixed at 20% for all the emulsions considered here. Various viscosity grades of silicone oils were used as a dispersed phase. The formulations of emulsions used in the experimental runs are listed in Table 1. In the case of stabilized emulsions, nonionic surfactants, namely Span 40 (sorbitan monopalmitate, F.W. 403, Sigma), Tween 60 (polyoxyethylene(20) sorbitan monostearate, F.W. 1311, Aldrich) and Pluronic L64 (block copolymer of ethylene oxide and propylene oxide, $M_w = 2900$, BASF) were used in order to prevent the electroviscous effect caused by charges dissolved from surfactants. Each nonionic surfactant was dissolved in castor oil. Due to the low solubility of Span 40 in castor oil, the limited range of the surfactant concen-

Table 1. Physical properties of emulsions used in the experiments

	Formulation Dispersed phase / continuous phase	Viscosity ratio, λ	Conductivity ratio	Average drop size (μm)
NS1	Silicone oil[a] (μ = 1.29Pa.s) / castor oil	0.83	0.153	31.10
NS2	Silicone oil[b] (μ = 1.09Pa.s) / castor oil + 2 wt% ethyl alcohol	0.64	0.004	-
SP1	Silicone oil (μ = 1.29Pa.s) / castor oil + Span 40 0.005M	0.90	0.126	23.55
SP2	Silicone oil (μ = 1.29Pa.s) / castor oil + Span 40 0.05M	0.92	0.071	15.94
PL1	Silicone oil (μ = 1.29Pa.s) / castor oil + PL64 0.05M	0.81	0.005	26.14
TW1	Silicone oil (μ = 1.29Pa.s) / castor oil + Tween 60 0.05M	0.92	0.003	31.45
PL2	Silicone oil[c] (μ = 4.03Pa.s) / castor oil + PL64 0.05M	2.54	0.005	-
TW2	Silicone oil (μ = 4.03Pa.s) / castor oil + Tween 60 0.03M	2.64	0.004	-

[a] 5.8 × 10⁻¹² $\Omega^{-1}m^{-1}$
[b] 5.8 × 10⁻¹² $\Omega^{-1}m^{-1}$
[c] 5.3 × 10⁻¹² $\Omega^{-1}m^{-1}$

tration was considered. The solubilities of Tween 60 and Pluronic L64 in castor oil were quite good, but the electrical properties, especially conductivities of the surfactant solutions were increased considerably. As noted in our previous study [Ha and Yang (1999)], when the conductivity of the continuous phase is increased, the negative viscosity effect is largely eliminated. Thus, we only considered dilute solutions of Tween 60 and Pluronic L64 in order to produce the considerable negative viscosity effect.

The conductivities of the liquids used for preparation of emulsions were measured by a parallel plate fixture of 1mm gap and a sensitive ammeter. After the field was applied, the electric current was measured by the ammeter. The measured current was divided by the area of the plate to give the current density. The conductivities were then obtained by dividing the current density by the electric field strength. The repeated measurements of conductivities at various electric field strengths showed that the conductivities remained nearly constant in the electric field range considered here.

The rheological responses of the constituent fluids and emulsions were measured by an ARES fluid rheometer (Rheometric Scientific) with or without an electric field. The parallel plate fixture of 5cm in diameter was used. The gap between upper and lower plates was 1mm. High voltage dc power supply (Glassman High Voltage, series EH) was connected to the upper and lower plates, which worked as electrodes. The ER responses of emulsions were measured at room temperature (23±1°C).
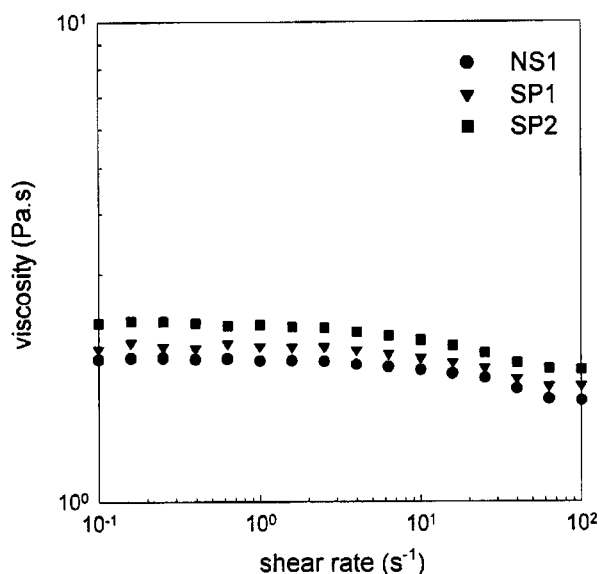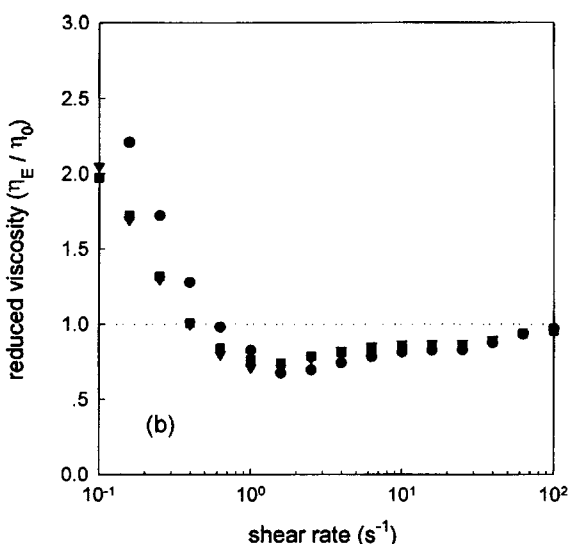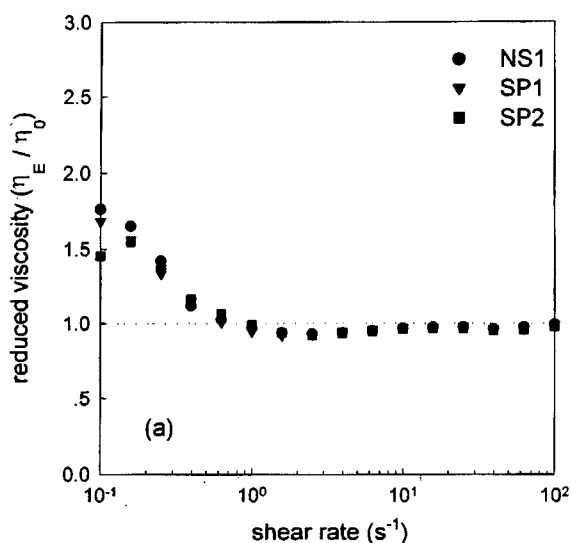
3. Results and discussion

Fig. 1 Rheological behavior of surfactant-free (NS1) and stabilized (SP1 and SP2) emulsions in the absence of an electric field.

In Fig. 1, the viscosity versus shear rate for emulsions with or without Span 40 is shown in the absence of an electric field. All of the emulsions considered here exhibit Newtonian behavior in the presence or absence of the surfactant, although slight shear thinning effect can be observed at high shear rates. The shear viscosities of emulsions stabilized by the surfactant shifted to slightly higher values and the general features are preserved. This indicates that the presence of surfactant does not produce any considerable effect responsible for the non-Newtonian responses but merely reduced the size of the dispersed phase due to this low surfactant concentration. Consequently, the observed rheological responses of emulsions are solely to the electric field rather than any consequences of surfactant molecules.

The adsorbed film of surfactant at the interface between two fluid phases has rheological properties which are different distinctively from those of the fluid phases [Edwards et al. (1991)]. The primary role of surfactant molecules is to decrease the interfacial tension between the dispersed and the continuous phases producing the fine morphology of emulsion. Moreover, the surfactant molecules resided in the interface decreases the surface mobility of the suspended droplets, so that there would be less distortion and also less internal circulation within the droplets. When the droplets deform in a shear flow field, reduction in the particle size tends to increase the rigidity of the droplet due to either the capillary pressure or to the rigidity of a surfactant film. Evidently, this increases the emulsion viscosity. On the other hand, depending on the nature of interactions with the droplets, the interaction potential between the droplets is strongly influenced. For instance, adsorption and hydrolysis of the surfactant film may significantly enhance the steric repulsion by effectively increasing the drop size. In addition, it has been shown that the presence of free surfactants in the emulsion can cause the flocculate. The non-Newtonian behavior in emulsions is believed to occur due to the formation of flocs of dispersed droplets. When a floc of droplets is formed, it immobilizes a significant amount of the continuous phase within itself. Consequently, the effective dispersed phase concentration of a non-Newtonian emulsion is higher than its true concentration.
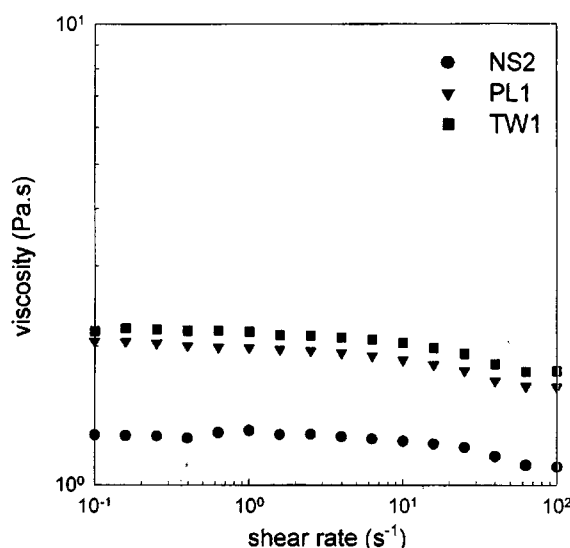
Fig. 2 shows that the rheological responses of emulsions stabilized by Span 40 in an electric field. As observed in our previous study [Ha and Yang (1999)], this type of emulsion exhibits three distinctively different responses depending on the relative strength of the shear flow and electric field; namely, the positive viscosity effect when the electric field is dominant, the negative viscosity effect when two driving forces are competing, and finally, no considerable ER effect when the shear flow is dominant. As can be seen from Fig. 2, the general feature of rheological responses is not changed compared with the surfactant-free

Fig. 2 Rheological behavior of surfactant-free (NS1) and stabilized (SP1 and SP2) emulsions in the presence of an electric field. (a) E = 0.8 kV/mm; (b) E = 1.6 kV/mm.

Fig. 3 Rheological behavior of surfactant-free (NS2) and stabilized (PL1 and TW2) emulsions in the absence of an electric field.

emulsions. When the electric field strength is relatively weak, there is no considerable difference between three types of emulsions considered here as shown in Fig. 2(a). However, the contribution from the added surfactant can be found more significantly as electric field strength increases. At the same electric field strength, the viscosity enhancement is slightly decreased as the surfactant concentration increases in low shear rates. Furthermore, although the effect is small, the viscosity reduction in intermediate shear rates decreases in the presence of the surfactant.

The effect of nonionic surfactants with much longer hydrophilic tail on the rheological behavior of emulsion is considered in Fig. 3 in the absence of an electric field. In this case, the surfactant molecules act effectively as an emulsifier. It is anticipated that the size of dispersed phase is greatly reduced due to the presence of the surfactant mole-

cules. Stabilized emulsions display very high viscosities compared with the surfactant-free emulsion of similar electrical properties. However, the generic feature of viscosity-shear rate relationship is not changed. There is no indication of any non-Newtonian characteristics or any differences except in the shear viscosities are generated by the stabilization of emulsion.

The electrorheological responses of emulsions are depicted in Fig. 4. Since the continuous phase has a considerably higher conductivity than the dispersed phase for each emulsion, the magnitude of negative viscosity effect is not appreciable as much as seen from the results included in Fig. 2. Nevertheless, the viscosity reduction induced by the nonionic surfactants is obvious. It is surprising that, although the drop size and its distribution are probably different from each other, the rheological responses of emulsions in an electric field can be described fairly in terms of the reduced viscosities. Moreover, it can be noted from Fig. 4(a) that the presence of the surfactant molecules diminishes the negative viscosity effect. When the electric field strength is increased, the effect of surfactants is appreciable in low shear rates. Meanwhile, the surfactants induce a negligible effect at high shear rates as can be seen clearly in Fig. 4(b).

The reason why the negative viscosity effect is suppressed in the presence of the surfactant may be explained as follows. Firstly, the surfactant molecules resided in the drop surface are able to inhibit the rotation of droplets, which is suggested as a reasonable cause of the viscosity reduction. Secondly, the rotation of small droplet requires a very high electric field strength compared with the large ones with the same electrical properties. It is expected that both the mechanisms act simultaneously in our experi-
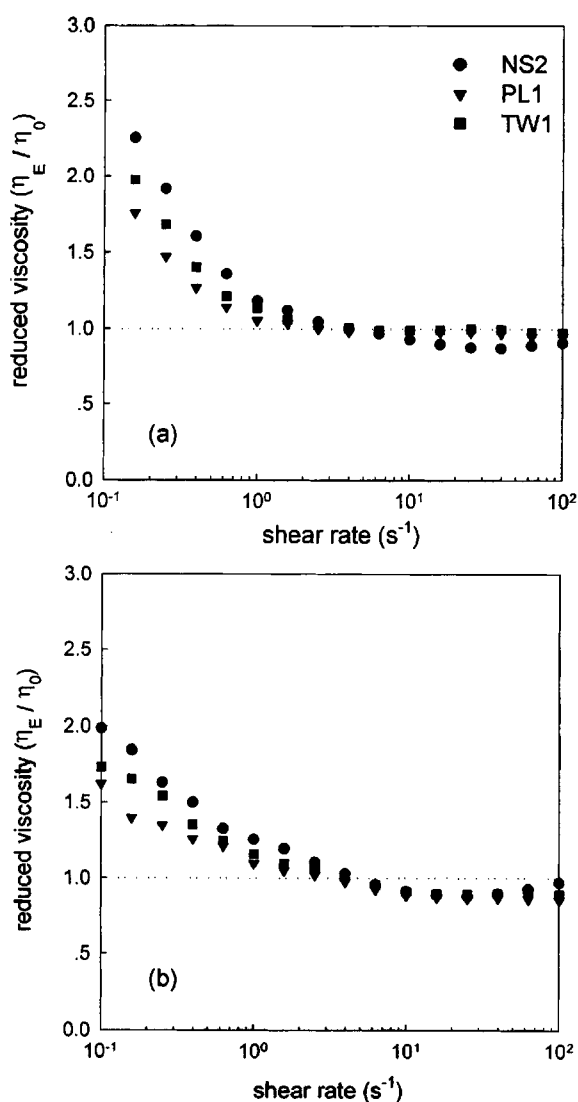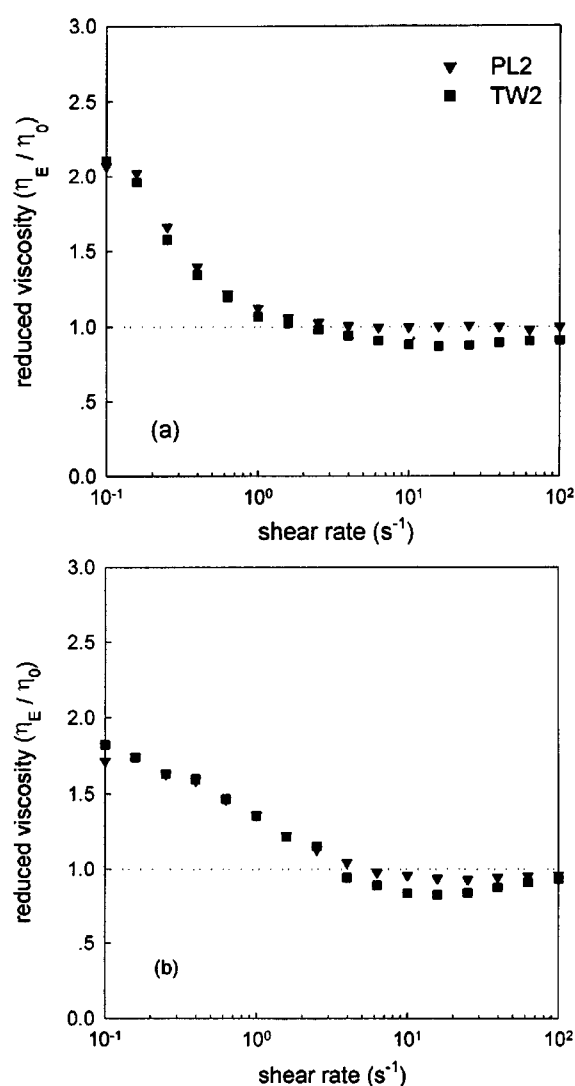
Fig. 4 Rheological behavior of surfactant-free (NS2) and stabilized (PL1 and TW1) emulsions in the presence of an electric field. (a) E = 0.8 kV/mm; (b) E = 1.6 kV/mm.

Fig. 5 Rheological behavior of stabilized (PL2 and TW2) emulsions in the presence of an electric field. (a) E = 0.8 kV/mm; (b) E = 1.6 kV/mm.

ments. However, at the present extent of knowledge, it is ambiguous which is the primary mechanism.

Also noted from Fig. 4(b) is that the positive viscosity effect is decreased due to the presence of the surfactant when the shear flow is weak. It is known that the positive viscosity effect is produced by the formation of chain-like morphology of dispersed phase due to the electropolarization between dispersed droplets. However, this chain-like morphology is awfully unstable, and thus, easily disturbed by increasing flow and/or electric field strength. Obviously, the steric hindrance caused by the surfactant molecules is unfavorable for the formation of electric-field-induced structures.

In order to understand the size effect of surfactant molecules more clearly, we consider emulsion systems having much higher viscosity ratios. This is because the greater

negative viscosity effect is produced in the case of the higher viscosity ratio. It is apparent that the surfactant molecules suppress the negative viscosity effect and the size of surfactant molecules is a nontrivial factor. Indeed, as seen from Fig. 5, for the larger and more surfactant molecules, the weaker negative viscosity effect is observed.

4. Conclusions

We have considered in this study the effect of nonionic surfactant molecules on the rheological responses of emulsion systems in a uniform dc electric field. Since the model emulsions are prepared by mixing the less conducting dispersed phase and the more conducting continuous phase, the negative viscosity effect is produced in the intermediate shear rate region. The positive viscosity effect is also

observed when the weak shear flow is imposed. The rheological responses of emulsions are influenced by the presence of the surfactant molecules in a few different ways. Firstly, the apparent viscosity of emulsion is enhanced by the reduced size of dispersed phase. In an electric field, the presence of the surfactant reduces both the positive and negative viscosity effects by preventing both the formation of chain-like morphology and the electrorotation of dispersed phase. The surfactant effect becomes the more appreciable for the larger hydrocarbon tails.

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