Control of Viscoelasticity Using Redox Reaction

Koji Tsuchiya,[†] Yoichi Orihara,[†] Yukishige Kondo,[‡,§] Norio Yoshino,[‡,§] Takahiro Ohkubo,[*,§]
Hideki Sakai,[*,†,§] and Masahiko Abe[†,§]

*Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan,
Faculty of Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan, and
Institute of Colloid and Interface Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku,
Tokyo 162-8601, Japan*

Received June 4, 2004; E-mail: hisakai@rs.noda.tus.ac.jp

Significant attention has recently been paid to the dynamic control of viscosity or viscoelasticity of fluids using external stimuli because this can be applied to clutches for transmission,[1] valves,[2] and precise control of mechanical position.[3] Electrorheological (ER) fluids[4−8] are colloidal dispersions, the viscosity of which can be controlled by applied electric potential. Application of an alternating electric field to conventional ER dispersions produces a viscosity rise mainly in the direction perpendicular to the field because the dispersed particles align to form strings in the direction parallel to the field because of the attraction of induced dipoles.[4] These conventional ER fluids, however, have some disadvantages from a viewpoint of industrial application because their stability is usually poor, and a high voltage (usually above 1 kV/mm) and a high dispersoid concentration (usually above 10 vol %) are required to gain a useful viscosity change.

We report a novel ER fluid whose viscoelasticity can be controlled using a "Faradaic (redox) reaction". Our system is based on a cationic "redox-switchable" ferrocenyl surfactant ((11-ferrocenylundecyl)trimethylammonium bromide, FTMA, Scheme 1) that self-assembles into wormlike micelles in the presence of sodium salicylate (NaSal). Wormlike micelles cause the system to exhibit a remarkable viscoelastic behavior as a result of the formation of a three-dimensional network consisting of entangled micelles.[9−12] Ferrocenyl surfactants permit control of formation and disruption of aggregates such as micelles[13−16] and vesicles[17−20] by their redox reactions. FTMA has a redox-active ferrocenyl group positioned at the end of its alkyl chain. The ferrocenyl group in the reduced form is hydrophobic, while the ferricinium cation (oxidized form) acts as a hydrophilic group. This causes a remarkable change in the hydrophilic−lipophilic balance of FTMA, thereby altering its aggregation state. We report here that it is possible to control the viscoelasticity of aqueous FTMA/NaSal mixtures by tuning the degree of entanglement of wormlike micelles through redox reaction of FTMA.

Figure 1a−c shows a photograph of the appearance of aqueous solutions containing mixtures of FTMA (reduced form, 50 mM)/ NaSal with molar ratios of C_{NaSal}/C_{FTMA} = 0, 0.2, and 0.4, respectively. Tilting of the solutions by 90° caused the solutions of FTMA alone (Figure 1a) and FTMA/NaSal mixture at C_{NaSal}/C_{FTMA} = 0.2 (Figure 1b) to flow immediately, whereas it produced no flow of the solution of the mixture at C_{NaSal}/C_{FTMA} = 0.4 (Figure 1c).

We then conducted dynamic viscoelasticity measurements at 25 °C on the mixture (C_{NaSal}/C_{FTMA} = 0.4) using a stress-controlled rheometer (CSL100, Carri-Med, Ltd.) equipped with a cone-plate type geometry. The mixture was found to be a non-Newtonian fluid.

Scheme 1. Redox Reaction of FTMA
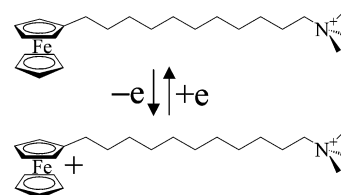

Figure 2 shows the storage modulus G′, the loss modulus G″, and the real part of the complex viscosity |η*| as a function of angular frequency ω. The G′ curve exhibited a definite plateau at high frequencies, and G″ was higher than G′ at low frequencies. The viscoelastic behavior is similar to that for wormlike micellar solutions of cetyltrimethylammonium bromide (CTAB), a typical cationic surfactant, with added NaSal.[9,10] The zero shear viscosity η_0 is given by $\lim_{\omega \to 0}|\eta^*|$. The value of η_0 obtained for the mixture was about 15 Pa·s, which is 4 orders of magnitude higher than the viscosity of water (about 1×10^{-3} Pa·s).
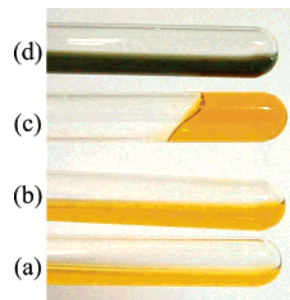

Figure 1. Photograph showing the appearance of aqueous FTMA(50 mM)/ NaSal mixture tilted by 90°. Samples a, b, and c are aqueous FTMA(reduced form)/NaSal mixtures at molar ratios of C_{NaSal}/C_{FTMA} = 0, 0.2, and 0.4, respectively. Sample d is an aqueous FTMA/NaSal mixture (C_{NaSal}/C_{FTMA} = 0.4) after electrolytic oxidation.
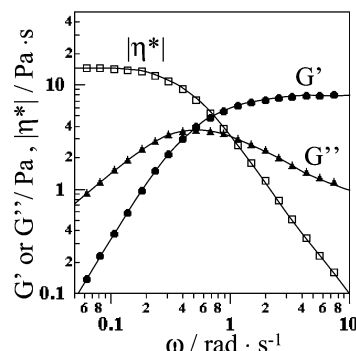

Figure 2. Storage modulus G′, loss modulus G″, and the real part of the complex viscosity |η*| as a function of angular frequency ω for aqueous FTMA (reduced form)/NaSal mixture (C_{NaSal}/C_{FTMA} = 0.4).

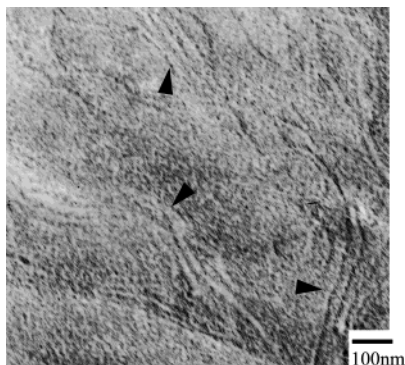[†] Faculty of Science and Technology.
[‡] Faculty of Engineering.
[§] Institute of Colloid and Interface Science.

Figure 3. Freeze−fracture TEM micrograph of aqueous FTMA (reduced form)/NaSal mixture ($C_{NaSal}/C_{FTMA} = 0.4$).

Figure 4. Schematic representation of aggregates formed in (a) aqueous FTMA(reduced form)/NaSal mixture ($C_{NaSal}/C_{FTMA} = 0.4$) and (b) aqueous FTMA(oxidized form)/NaSal mixture ($C_{NaSal}/C_{FTMA} = 0.4$).

The aggregation state of the mixture was investigated by freeze−fracture transmission electron microscopy (FF-TEM). Extremely elongated wormlike micelles that are flexible and entangled with each other were observed on the FF-TEM micrograph (Figure 3). These aggregates had diameters of 8 nm and lengths in the micrometer range. The high viscoelasticity observed for the mixed solution can therefore be ascribed to an entangled network of wormlike micelles of FTMA.

This highly viscoelastic aqueous FTMA/NaSal mixture (Figure 1c) was electrolyzed with a three-electrode system at 25 °C. A platinum plate (8.64 cm^2), platinum wire, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. An aqueous NaSal solution at 20 mM, the same concentration as that in the sample solution, was used as the supporting electrolyte to prevent the change in aggregation state. Electrolytic oxidation was performed on the aqueous mixture at +0.5 V vs SCE, a potential much more positive than the equilibrium potential (+0.15 V vs SCE) of FTMA,[13] with a potentiostat (model HA-301, Hokuto Denko Co.) for 24 h while the solution was bubbled with N$_2$ and stirred. The reaction on the counter electrode is the reduction of water.

When the samples were tilted by 90°, the oxidized mixture easily flowed (Figure 1d) while the reduced sample hardly flowed (Figure 1c). We then examined the viscoelastic behavior of the oxidized mixture with a double-concentric cylinder-type rheometer. The shear stress was proportional to the shear rate, and no hysteresis was observed between the flow curves obtained by increasing and then decreasing shear rate. The oxidized sample is therefore a Newtonian fluid with no elasticity, and its viscosity has a value of 2.5×10^{-3} Pa·s, which is about "1/6000" of the zero shear viscosity of the reduced sample. This remarkable viscoelasticity decrease is caused by a significant change in the aggregation state of the mixture, that is, from wormlike micelles to monomers and/or other smaller aggregates, probably short rodlike micelles. Abbott et al. reported the absence of micellization upon concentrations of 30 mM for the oxidized FTMA compared with a critical micelle concentration (cmc) of 0.07 mM for reduced FTMA.[21] This suggests the dissolution into monomers of a portion of the molecules forming wormlike micelles upon their oxidation. The number of aggregates formed in the mixture decreases, and elliptic aggregates whose length is much shorter than wormlike micelles are likely to be formed after oxidation of the surfactant. Because the entanglement of elliptic aggregates to form a network is unlikely to occur, a large decrease in visc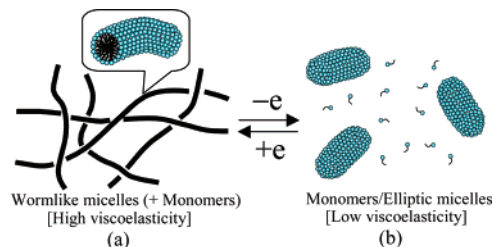oelasticity was induced by oxidation. Figure 4 shows a schematic representation of aggregates formed in the reduced and oxidized aqueous FTMA/NaSal mixtures.

The present method of viscoelasticity control has several advantages over conventional ER fluids. We can significantly decrease the viscoelasticity (6000 times) of aqueous dilute FTMA/NaSal solutions ($C_{FTMA} = 2.3$ wt %) by applying an extremely low DC voltage (+0.5 V vs SCE). The system reported in this communication is a promising candidate for new ER fluid that will widely be applied to ink for inkjet printers and the controlled release of substances such as dyes and perfumes. The principal finding we report here can be also generalized to other external stimuli that can be used to switch the properties of surfactant systems. For example, we have also demonstrated photochemical control of viscoelasticity in an aqueous mixture of a cationic surfactant modified with a "photoswitchable" azobenzene moiety and NaSal. This result will be reported elsewhere soon.

Supporting Information Available: Preparation of aqueous FTMA/NaSal mixtures, freeze−fracture TEM method, UV−vis spectra before and after electrolytic oxidation, rheological behavior after electrolytic oxidation, and reversible control of rheological behavior. This material is available free of charge via the Internet at http://pubs.acs.org.

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