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Manipulation of the viscosity behavior of wormlike micellar gels by changing the molecular structure of added perfumes

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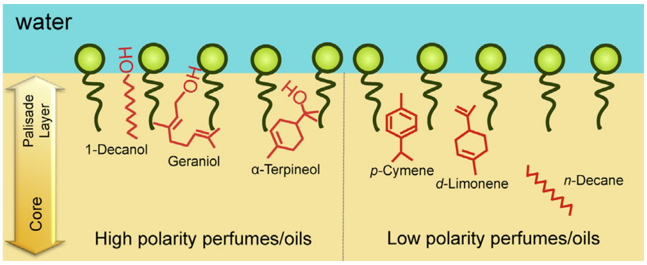
HIGHLIGHTS

- Significant effect of perfume solubilization on viscosity of wormlike micellar solutions.
- Smaller penetration in palisade layer for branched or cyclic high polarity molecules.
- Larger penetration in palisade layer for branched or cyclic low polarity molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

We studied the effect of a trace amount of perfumes and oils on the rheological properties of micellar solutions formed in a water/sodium dodecyl sulfate (SDS)/tri(oxyethylene) dodecyl ether ($C_{12}EO_3$) system which gives a maximum zero-shear viscosity as a function of surfactant mixing fraction due to wormlike micelle formation. By adding high-polarity perfumes and oils (9-decen-1-ol, 1-decanol, *l*-menthol, geraniol and α-terpineol), the viscosity peak shifts to lower hydrophobic surfactant composition and the degree of the viscosity peak shift is the largest for the linear-chain molecules and smaller for the branched or cyclic molecules. Dynamic frequency tests show that the zero-shear viscosity behavior for different high-polarity perfume and oil systems varies due to the change in the relaxation time behavior. The linear-chain molecules can penetrate well in the palisade layer of micelles and the penetration could be interrupted by branched or cyclic molecular architecture. On the other hand, by adding low-polarity perfumes and oils (*p*-cymene, hexahydrocumene, butylbenzene, *d*-limonene and decane), the behavior of the viscosity curve is quite different for decane and for other molecules, i.e. decane decreases the viscosity peak without shift of surfactant mixing fraction whereas other molecules behave as high-polarity molecules.

1. Introduction

It is well known that the micelles in aqueous solutions of surfactants grow one-dimensionally by tuning surfactant hydrophobically, and long flexible aggregates called wormlike micelles are produced. Because of entanglement of the wormlike micelles, its solution shows highly viscoelastic properties. Unlike polymers, wormlike micelles can break and reform under shear. Therefore they can be used for drag reduction (DR) agents for fluid transportation.

The formation of wormlike micelles has been reported in some ionic surfactant systems with the addition of salts [1–4] and mixed hydrophilic–lipophilic or anionic–cationic surfactant systems [5–9]. Recently, it was found that several anionic and nonionic surfactants form wormlike micelles with nonionic cosurfactants [10–17]. Such mixed surfactant systems have good detergency and give good foamability. Especially foamability is related to the wormlike micelle formation since increased viscosity

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interrupts water drainage from foam. Therefore manipulating wormlike micelles in mixed surfactant systems is very important for constructing formulation of household and personal care products.

Viscosity of micellar solution of a hydrophilic surfactant system gradually increases by adding lipophilic surfactant and steeply increases above a certain mixing composition due to formation of wormlike micelles. With more increasing lipophilic composition, the viscosity reaches a maximum and decreases below phase separation composition due to branched micelle formation [18]. Such viscosity behavior of wormlike micellar solutions is highly influenced by a trace amount of oil solubilization. Rodrigues et al. [19] reported that the viscosity curve against hydrophilic–lipophilic mixing composition varied depending on molecular structure of oil solubilized. In case of a linear alkane, only maximum viscosity value decreased while the mixing composition giving the viscosity maximum. On the other hand, solubilization of an aromatic hydrocarbon changes the surfactant mixing fraction giving maximum solution viscosity while the maximum viscosity value is almost unchanged. Above difference in viscosity behavior is dependent on the difference in the solubilization site in micelles. Most of the household and personal care products contain perfumes which are normally water-insoluble and can be solubilized in micelles. Also the chemical structure of perfumes has a lot of variety, which affects the solubilization site. Therefore, in this paper, we studied the effect of adding various perfumes molecules with different chemical structures on the viscosity behavior of wormlike micellar solutions.

2. Experimental

2.1. Materials

Homogeneous tri(oxyethylene) dodecyl ether ($C_{12}EO_3$) was purchased from Nikko Chemicals Co. (Japan). Sodium dodecyl sulfate (SDS, 99%) was purchased from Sigma–Aldrich Co. (USA). α-Terpineol (>95%), *p*-cymene (>95%), 9-decen-1-ol (>95%), 1-decanol (>97%), hexahydrocumene (>99%) and butylbenzene (>99%) from Tokyo Kasei Kogyo (Japan) and *l*-menthol (>98%), geraniol (99%), *d*-limonene (>95%) and decane (99%) from Kanto Chemical Co., Ltd. (Japan) were also used. All materials were used without further purification.

Deionized (Millipore filtered) water was used to prepare the samples.

2.2. Sample preparation

The water concentration was fixed at 90 wt% (10 wt% total surfactant). The perfume (oil) was added 0.5 wt% to an aqueous solution of surfactant, respectively. Sealed ampoules containing the required amounts of components were homogenized and kept in a thermostated bath at 25 °C for at least 24 h before the measurements.

2.3. Rheological measurements

The rheological measurements were performed in an AR-G2 rheometer (TA Instruments, USA) using cone-and-plate geometry with an angle of 1°. We have used two different geometry with diameter 60 and 40 mm, depending on the viscosity of the samples. Plate temperature was controlled by a peltier unit at 25 °C. Dynamic frequency sweep measurements were performed in the linear viscoelastic regime, as determined previously by dynamic strain sweep measurements.

3. Results

3.1. Effect of perfume solubilization on viscosity behavior

SDS is a hydrophilic surfactant and forms spherical micelles in water and the solution viscosity is not so high. Acharya et al. [14] reported a viscosity increase by mixing a hydrophobic nonionic surfactant, $C_{12}EO_3$ in an aqueous SDS solution. The solution viscosity in the water/SDS/$C_{12}EO_3$ system gradually increases at low $C_{12}EO_3$ composition but drastically above a certain composition, which is attributed to entanglement of wormlike micelles. However the solution viscosity decreases with further increase in the hydrophobic surfactant composition due to formation of branched-network micelles before reaching the phase separation composition.

In the present study, we solubilized 0.5 wt% of perfumes and other oils in the above-mentioned water/SDS/$C_{12}EO_3$ system in which the surfactant concentration is kept at 10 wt%. Perfumes and oils were fully solubilized in the SDS-$C_{12}EO_3$ micelles. We did steady rheological measurements for the perfume (or oil) added systems at 25 °C at different surfactant mixing compositions. Fig. 1(a) is the result of the geraniol-added system. Viscosity is almost constant at low shear rate and it goes down above certain shear rate above $X = 0.50$, where X indicates the mole fraction of $C_{12}EO_3$ in total surfactants (SDS + $C_{12}EO_3$). Such a shear thinning behavior is typically observed for wormlike micellar solutions. The break point of the viscosity curve shifts to lower shear rate when X increases from 0.50 to 0.60 and it goes to opposite direction above $X = 0.62$, where X indicates the mole fraction of $C_{12}EO_3$ in total surfactants. Similar behavior is observed in the *d*-limonene system (Fig. 1(b)), other perfume and oil systems, and also for the oil-free system [14].

Fig. 2 is a plot of zero shear viscosity (η_0) for high-polarity perfumes and oils (see Table 1(a)) systems against X. The oil-free system shows an increase in viscosity with increasing $C_{12}EO_3$

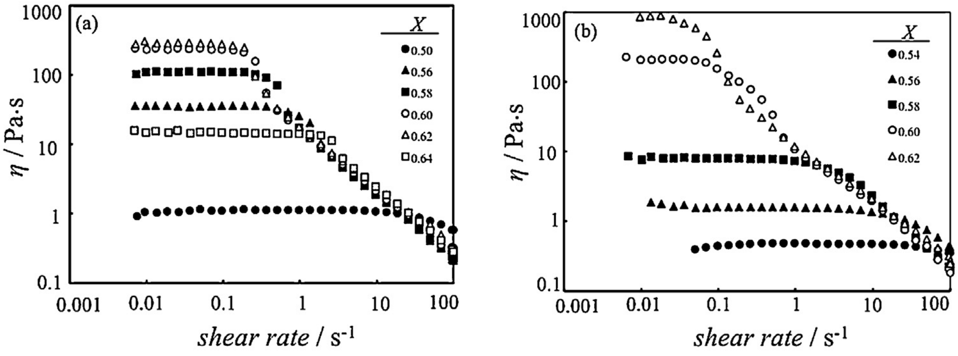

Fig. 1. Plot of viscosity for micellar solutions of the (a) water/SDS/$C_{12}EO_3$/geraniol and (b) water/SDS/$C_{12}EO_3$/*d*-limonene systems at 25 °C against shear rate at various mole fraction of $C_{12}EO_3$ in total surfactants (X) is shown.