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ORIGINAL CONTRIBUTION

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Vesicle formation in oleyldimethylamine oxide/sodium oleate mixtures

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Abstract Vesicle formation in a mixture of oleyldimethylamine oxide (OleylDMAO) and sodium oleate (NaOl) was investigated by viscoelastic measurements and cryoscopic transmission electron micrograph (cryo-TEM) observations. The viscoelastic properties changed with increasing mole fraction of NaOl (X_{NaOl}) from the Maxwell behavior of OleylDMAO solutions ($X_{\mathrm{NaOl}}=0$) suggesting a transient network of long flexible chains. For $X_{\mathrm{NaOl}}=0.2$ and 0.4 mixtures, both the shear storage modulus G' and the shear loss modulus G'' showed weak dependences on angular frequency ω with a relation $G'>G''$. From cryo-TEM observations, vesicles coexisted with threadlike micelles in mixtures of $X_{\mathrm{NaOl}}=0.2$ and 0.3. As X_{NaOl} increased further ($X_{\mathrm{NaOl}}=0.5$ and 0.6), threadlike micelles disappeared and the coexistence of vesicles and globular micelles was observed. At $X_{\mathrm{NaOl}}=0.5$, the viscosity decreased remarkably, which was consistent with the disappearance of threadlike micelles. The results indicated that vesicles were formed by the addition of NaOl to OleylDMAO solutions, contrary to the expectation of a decrease of the packing parameter with the introduction of electric charges.

Keywords Oleyldimethylamine oxide · Sodium oleate · Complex formation · Vesicles · Threadlike micelles

Introduction

Soaps have advantages over synthetic detergents with respect to toxicity and biodegradability. In aqueous media, soaps are known to form acid soaps on partial protonation [1]. It has been reported that vesicles are formed by protonation of sodium oleate (NaOl) [2, 3]. Mixtures of NaOl with alkyltrimethylammonium bromide (C*n*TMAB) have been investigated. It was reported that entangled threadlike micelles were formed in NaOl/C8TMAB mixtures. For NaOl/C10TMAB and NaOl/C12TMAB mixtures, formation of vesicles was suggested in a certain range of the mole ratio [4].

In equimolar mixtures of amine oxide and NaOl, catanionic complex formation between protonated amine oxide and oleate anion has been reported [5]. For mixtures containing alkyldimethylamine oxides (C*n*DMAO), such as C16DMAO, C14DMAO, and C12DMAO, both the pH values of the mixtures and the amount of catanionic complex increased with the chain length of amine oxide. For the mixture of C12DMAO and oleate, an attractive interaction between the headgroups is suggested by the interaction parameter $\beta=-3.9$ from the cmc measurement [6].

In mixed surfactant systems, synergisms such as the lowering of the cmc, enhanced surface activities, the formation of vesicles, and micelle growth have been widely investigated [7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. Interaction between the headgroups of surfactants is important for the synergism. For example, in mixtures of anionic and cationic surfactants with attractive interaction between headgroups, micelle growth and vesicle formation were observed [7, 8]. Several contributions responsible for the synergism have been examined [9]. Mixed systems of the nonionic C*n*DMAO with ionic surfactants have been investigated, such as sodium dodecyl sulfate (SDS) [10, 11, 12, 13], potassium dodecanesulfonate [14], calcium dodecyl sulfate ($Ca(DS)_2$) [15], sodium dodecylbenzenesulfonate [16], or C*n*TMAB [10, 11]. The zero shear viscosity of the mixture of oleyldimethylamine oxide (OleylDMAO) and SDS increases first and then decreases with increasing SDS fraction [11]. For a C12DMAO/SDS mixture, the interaction parameter β of the regular solution theory (RST) is −1.7 [10]. A mixture of C14DMAO and $Ca(DS)_2$ is reported to form vesicles [15].

In the present study, the viscoelastic properties and cryo-TEM observations of a mixture of OleylDMAO and NaOl are examined. It is expected that an attractive interaction between the headgroup of the amine oxide and that of NaOl induces complex formation, which increases the packing parameter and promotes structural changes.

Experimental

Materials

Oleyldimethylamine oxide was obtained from oleyldimethylamine (Lion Akzo) through oxidation in ethanol by hydrogen peroxide following, in most parts, a procedure reported previously [17]. Sodium oleate samples were prepared by neutralization (in ethanol) of highly pure oleic acid (purity 99.999%), from Research Institute of Biological Materials Japan, Ltd. The total surfactant concentration C_d was expressed in mol kg^{-1}.

Methods

Dynamic viscoelastic and shear flow measurements were performed with a stress-controlled rheometer (CarriMED CSL-100, England) with a cone plate (plate diameter 6 cm, 2° angle). The storage modulus G' and the loss modulus G'' were measured as functions of angular frequency ω from 0.01 to 60 rad s^{-1} at a temperature of 25 °C. The dynamic measurements were made at strain amplitude levels where the dynamic moduli are strain independent. The rheometer was equipped with a solvent trap to protect the sample from solvent evaporation. Solutions were kept for at least 3 days before measurements. The temperature was controlled within 0.1 °C.

Results and discussion

Viscoelastic properties

Figure 1 shows the angular frequency ω dependence of the shear storage modulus G' and the shear loss modulus G'' of OleylDMAO solutions at $C_d = 50$ and 30×10^{-3} mol kg^{-1}. The viscoelastic behavior of OleylDMAO solutions at both concentrations can be well described with the Maxwell model [18], that is, the characteristic behavior of a transient network consisting of long flexible chains [11, 19, 20]. The slowest relaxation process is well separated from other processes (at higher frequency range) and the relaxation time is about 1 s, which is independent of the surfactant concentration in the range examined. It has been interpreted that the slowest relaxation of entanglement of threadlike micelles originates from scission and re-formation of the micelles [19, 20]. In a high-frequency range ($\omega > 10$ rad s^{-1}), on the other hand, the G' and G'' increase with frequency at $C_d = 30\times10^{-3}$ mol kg^{-1}. It is considered that the relaxation processes at the high-frequency side are associated with the motion of the threads between two entanglement points [21].

Adding a small amount of NaOl to the OleylDMAO solution changes the viscoelastic properties dramatically. Figure 2 shows the angular frequency ω dependence of G' and G'' of OleylDMAO/NaOl mixtures at $C_d = 50\times10^{-3}$ mol kg^{-1} at different mole fractions of

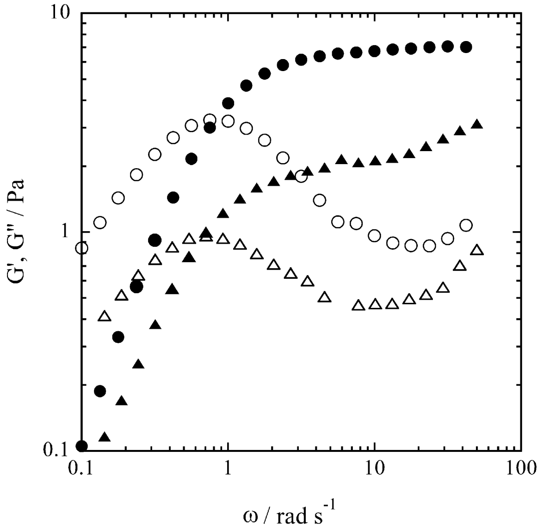

Fig. 1 Angular frequency ω dependence of the shear storage modulus G' (●, ▲) and shear loss modulus G'' (○, △) of OleylDMAO solutions ($X_{NaOl} = 0$) at 25 °C. *Circles* and *triangles* refer to the solutions at $C_d = 50$ and 30×10^{-3} mol kg^{-1}, respectively

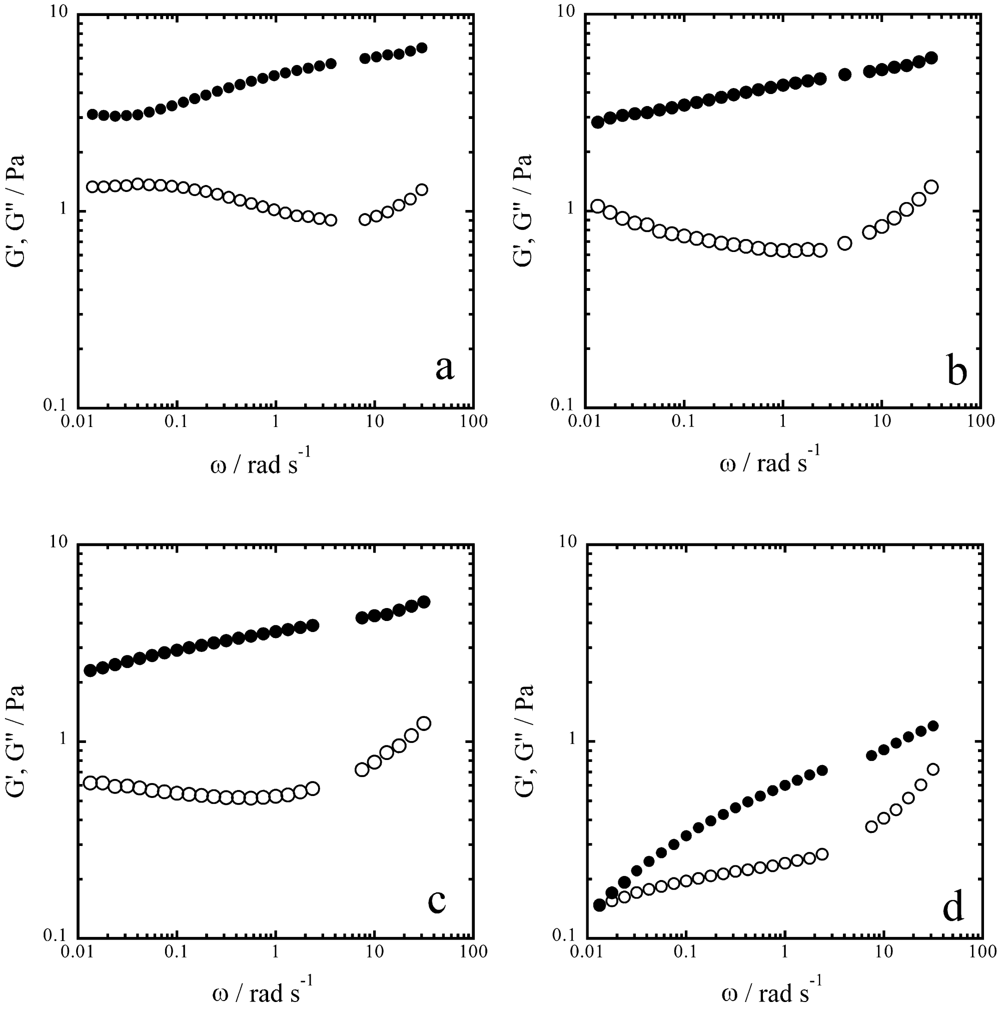

Fig. 2a–d Angular frequency ω dependence of the shear storage modulus G' (●) and shear loss modulus G'' (○) of Oleyl-DMAO/NaOl mixtures at 25 °C and $C_d = 50\times10^{-3}$ mol kg^{-1} at different mole fractions of NaOl (X_{NaOl}). **a** $X_{\mathrm{NaOl}} = 0.1$, **b** $X_{\mathrm{NaOl}} = 0.2$, **c** $X_{\mathrm{NaOl}} = 0.4$, and **d** $X_{\mathrm{NaOl}} = 0.5$

NaOl, X_{NaOl}, which is defined as NaOl/(NaOl + OleylDMAO). For a composition of $X_{\mathrm{NaOl}} = 0.1$, the Maxwell-type behavior characteristic of simple entangled threadlike micelles disappears (Fig. 2a). The values of G'' increase as the frequency decreases in the low-frequency side. At a lower frequency range, it is expected that the G'' will show a maximum, although it cannot be observed in the frequency range examined. On the other hand, the G' value weakly depends on the frequency and the plateau modulus was not observed clearly. These dynamic viscoelastic behaviors suggest that the mixture at $X_{\mathrm{NaOl}} = 0.1$ has a relaxation time distribution which is longer than that of $X_{\mathrm{NaOl}} = 0$. It should be noted that the Maxwell behavior of OleylDMAO solution ($X_{\mathrm{NaOl}} = 0$) is maintained at a low concentration of $C_d = 30\times10^{-3}$ mol kg^{-1}. This indicates that the change of the viscoelastic properties between $X_{\mathrm{NaOl}} = 0$ and 0.1 is not caused by a decrease in the nonionic OleylDMAO concentration, but is an effect arising from the addition of NaOl to OleylDMAO solution. For the $X_{\mathrm{NaOl}} = 0.2$ and 0.4 mixtures, both G' and G'' show weak dependences on the angular frequency with a relation $G' > G''$ in the frequency range examined here (Fig. 2b, c), and the Maxwell-type behavior characteristic of entangled threadlike micelles was not observed as similar to the $X_{\mathrm{NaOl}} = 0.1$ mixture. This suggests that other structures with another relaxation mechanism, such as branched threadlike micelles and vesicles, are formed by the addition of NaOl to OleylDMAO solution, which leads to a distribution of the relaxation times. For $X_{\mathrm{NaOl}} = 0.5$, the solidlike viscoelastic properties disappear as shown in Fig. 2d. From the above results, it is suggested that the aggregate structures change from the entangled threadlike micelles ($X_{\mathrm{NaOl}} = 0$) to another aggregate structure by the addition of NaOl to OleylDMAO solutions. The cryo-TEM observations (Fig. 5) revealed that, for $X_{\mathrm{NaOl}} = 0.2$ and 0.3, the vesicles and the branched threadlike micelles are formed beside the linear threadlike micelles and that for $X_{\mathrm{NaOl}} = 0.5$ and 0.6, the vesicles coexist with the globular micelles.

Figure 3 shows the shear rate dependence of the viscosity η obtained from the flow measurements. In the

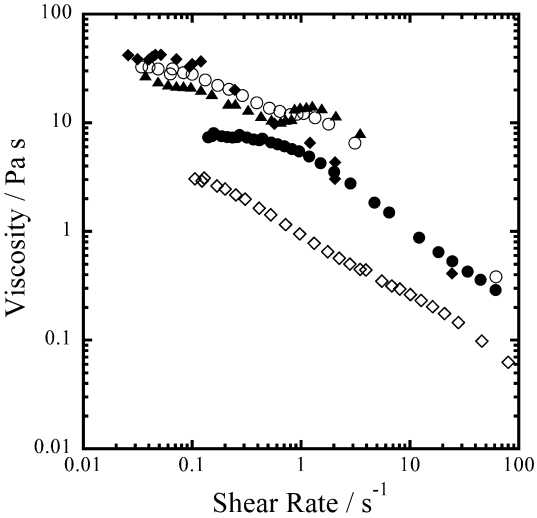

Fig. 3 Shear rate dependence of the viscosity of OleylDMAO/NaOl mixtures at 25 °C and $C_d = 50 \times 10^{-3}$ mol kg^{-1} with different values of X_{NaOl}. Symbols are: ●, $X_{\mathrm{NaOl}} = 0$; ◆, $X_{\mathrm{NaOl}} = 0.1$; ○, $X_{\mathrm{NaOl}} = 0.2$; ▲ $X_{\mathrm{NaOl}} = 0.4$; and ◇, $X_{\mathrm{NaOl}} = 0.5$

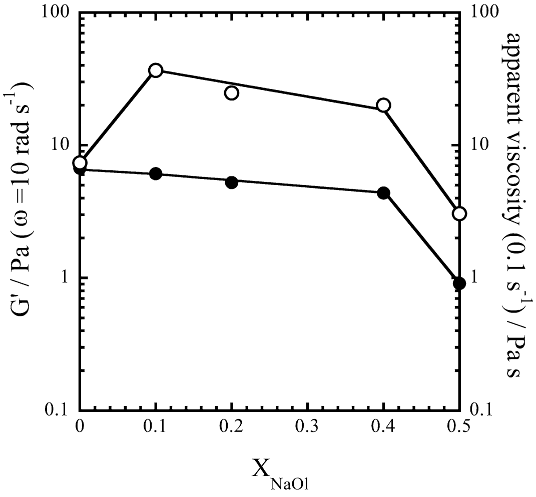

Fig. 4 The X_{NaOl} dependence of the apparent viscosity η (○) at 0.1 s^{-1} and the shear storage modulus G' (●) at $\omega = 10$ rad s^{-1} for OleylDMAO/NaOl mixtures at 25 °C and $C_d = 50 \times 10^{-3}$ mol kg^{-1}

solution consisting of long flexible chains ($X_{\mathrm{NaOl}} = 0$), the plateau viscosity was observed clearly at low shear rates and the solution showed a shear thinning behavior above 0.5 s^{-1}. For the mixtures of $X_{\mathrm{NaOl}} = 0.1$, 0.2, 0.4, and 0.5, the plateau viscosities were not observed in the range of low shear rates examined. For $X_{\mathrm{NaOl}} = 0.2$ and 0.4, an increase in the viscosity was observed around 1 s^{-1} of shear rate (shear thickening). Figure 4 shows the X_{NaOl} dependence of the storage modulus G' at $\omega = 10$ rad s^{-1} and the apparent viscosity at 0.1 s^{-1} of shear rate. The value of G' was nearly independent of the composition up to $X_{\mathrm{NaOl}} = 0.4$ and it significantly decreased at $X_{\mathrm{NaOl}} = 0.5$. The apparent viscosity increased at $X_{\mathrm{NaOl}} = 0.1$ and decreased slightly between $X_{\mathrm{NaOl}} = 0.1$ and 0.4, but it decreased remarkably at $X_{\mathrm{NaOl}} = 0.5$ due to the disappearance of the threadlike micelles.

Cryo-TEM micrograph

Figure 5a–d presents cryo-TEM pictures of OleylDMAO/NaOl mixtures ($C_d = 50 \times 10^{-3}$ mol kg^{-1}) at $X_{\mathrm{NaOl}} = 0.1$ (a), 0.2 (b), 0.3 (c), and 0.5 (d). The samples were incubated for about 1 month before the measurements. In the solutions of $X_{\mathrm{NaOl}} = 0.1$, very long threadlike micelles with few branching points were found, as shown in Fig. 5a. Many of the threadlike micelles extend over a micrometer without any branching. The small thickness of the film and the shear applied on blotting of the samples explains the orientation of the long structures. Vesicles in coexistence with threadlike micelles were observed in the mixture of $X_{\mathrm{NaOl}} = 0.2$, as shown in Fig. 5b. The size of the vesicles is mainly in the range of 20–50 nm radius. Compared with the case of $X_{\mathrm{NaOl}} = 0.1$, the threadlike micelles appear to branch more frequently. In the cryo-TEM picture at $X_{\mathrm{NaOl}} = 0.3$ (Fig. 5c), both vesicles and threadlike micelles were observed. The picture shows both long and short micelles and micelles closed to loops or branched. In this micrograph, and also in Fig. 5b, one may observe several dark dots that are interpreted as (parts of) elongated micelles oriented perpendicular to the film surface, i.e., parallel to the electron beam, which increases the contrast. For $X_{\mathrm{NaOl}} = 0.5$, relatively large vesicles, compared with $X_{\mathrm{NaOl}} = 0.2$ and 0.4, and globular micelles were observed (Fig. 5d). At $X_{\mathrm{NaOl}} = 0.6$, there are globular micelles and vesicles, and some open bilayer structures (not shown). It has been reported that vesicles in coexistence with globular micelles are observed in binary surfactant mixtures of alkanediyl-α,ω-bis(dimethyldodecylammonium bromide) and dodecyltrimethylammonium bromide [22]. It is clear from the cryo-TEM observations that vesicles are formed by addition of NaOl to OleylDMAO solutions, which suggests that the surfactant packing parameter increases with the introduction of electric charges. Vesicle formation with increasing X_{NaOl} is attributed to complex formation between OleylDMAO and oleate anion by attractive interaction between the headgroups.

Phase behavior and morphological changes

The system of the OleylDMAO/NaOl mixture is similar to a mixture of a cationic and an anionic surfactant in that both the pure components in dilute solution form micelles in an L_1 phase, whereas an equimolar mixture

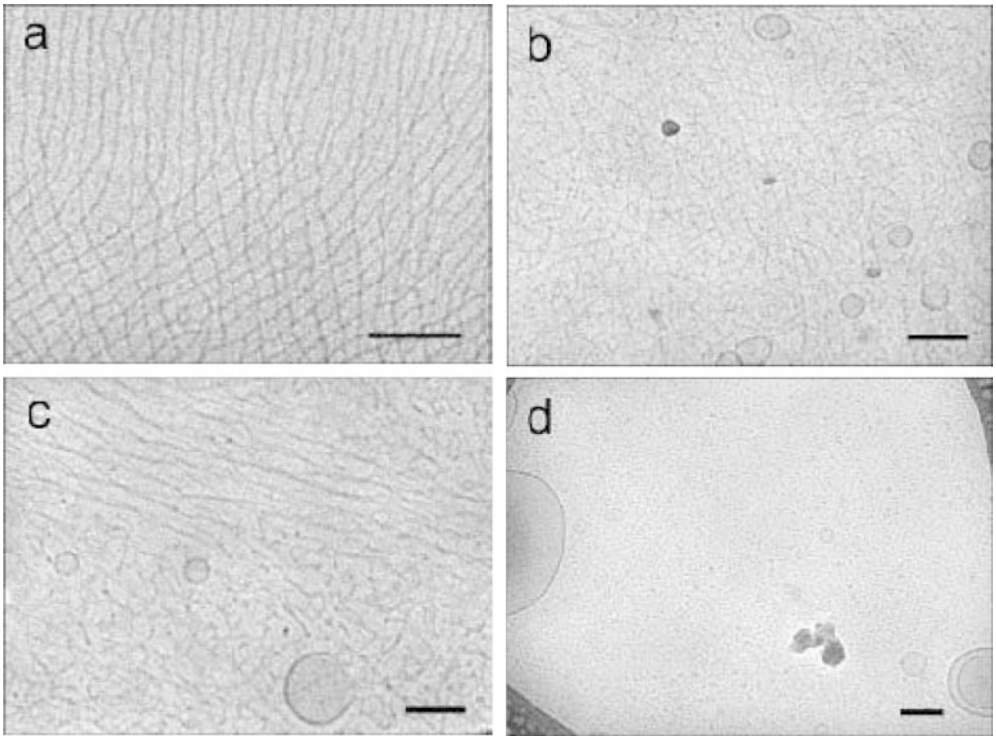

Fig. 5a–d Cryoscopic transmission electron micrographs of OleylDMAO/NaOl mixtures at $C_d = 50\times10^{-3}$ mol kg^{-1}. **a** $X_{NaOl} = 0.1$, **b** $X_{NaOl} = 0.2$, **c** $X_{NaOl} = 0.3$, and **d** $X_{NaOl} = 0.5$. A *bar* in each figure corresponds to 100 nm

preferentially gives bilayer structures with small curvatures. Long, threadlike micelles are formed by OleylDMAO itself. On addition of NaOl the border of the L_1 phase seems to be reached at a fraction of NaOl between 0.1 and 0.2; at the latter fraction there are already vesicle structures present (Fig. 5b). Vesicles from the L_α phase coexist with OleylDMAO-rich micelles at $X_{NaOl} = 0.3$. At $X_{NaOl} = 0.5$ and 0.6, vesicles are found together with globular micelles. The reason is probably that these micelles are NaOl-rich, belonging to the L_1 phase based on NaOl. The micelles in this phase in pure NaOl are known to be globular at low concentrations [3]. It is reasonable to assume that the lamellar phase at equal concentrations of the two surfactants is in equilibrium with an aqueous solution containing an excess of the surfactant with the highest cmc value, which in this case should be the ionic surfactant, forming globular micelles.

Conclusion

We found that vesicles were formed in the mixture of oleyldimethylamine oxide (OleylDMAO) and sodium oleate (NaOl) in $X_{NaOl} = 0.2$–0.6 mixtures. The viscoelastic properties changed on increasing the fraction of NaOl (X_{NaOl}) from the Maxwell behavior of OleylDMAO solutions ($X_{NaOl} = 0$) suggesting the transient network of long flexible chains. For $X_{NaOl} = 0.2$ and 0.4 mixtures, both the shear storage modulus G' and the shear loss modulus G'' showed weak dependences of angular frequency ω with a relation $G' > G''$. From cryo-TEM observations, vesicles coexisting with threadlike micelles were shown in mixtures of $X_{NaOl} = 0.2$ and 0.3. As X_{NaOl} increased further ($X_{NaOl} = 0.5$ and 0.6), threadlike micelles disappeared and the coexistence of vesicles and globular micelles was observed. It is expected that the globular micelles mainly consist of oleate anions. The results indicated that introduction of electric charges increased the packing parameter and hence induced a change from threadlike micelles to vesicles. Vesicle formation with increasing X_{NaOl} is attributed to complex formation between OleylDMAO and oleate anion, which was caused by attractive interaction between the headgroups.

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