Spontaneous Emulsification of Triolein Induced by Mixed Micellar Solutions of Sodium Polyoxyethylene Alkyl Ether Sulfate and Dodecyldimethyl Amine Oxide

Chika Endo\(^1\)\(^*\), Yoshiko Ito\(^1\), Chika Akabane\(^1\), Yukihiro Kaneko\(^1\) and Hideki Sakai\(^2\)

\(^1\) Functional Materials Science Research Laboratories, R & D, LION CORPORATION (7-2-1, Hirai, Edogawa-ku, Tokyo 132-0035, JAPAN)
\(^2\) Faculty of Science and Technology, Tokyo University of Science (2641 Yamazaki, Noda, Chiba, 278-8510, JAPAN)

Abstract: A new mechanism of spontaneous emulsification without any salts or co-solvents is described, and is related to the dilatational behavior. Spontaneous emulsification can reduce the time required to remove oily soils from hard surfaces and enhance the detergency, because this type of emulsification requires no external mechanical work. In this paper, we focused on triolein, the main component of food oils and human sebum soil, and tried to induce spontaneous emulsification by using mixed micellar solutions of sodium polyoxyethylene alkyl ether sulfate and N, N-dimethyldodecylamine oxide (AES/DDAO). We characterized the dilatation of the oil/water interface using dynamic interfacial tension and elasticity measurements. This study confirmed that the degree of spontaneous emulsification can be enhanced by controlling the molar ratio of DDAO to AES. This enhancement can be attributed to an increased rate of decrease in the dynamic interfacial tension (i.e., a decreased interface dilatational elasticity), allowing for much greater suppression of the Marangoni effect. Further, we determined that one of the reasons for the decrease in the interface dilatational elasticity is the increasing number of micelles near the oil drop interface, which results from a decrease in the electrostatic repulsion between the micelles and the drop interface. Therefore, controlling the molar ratio of a mixed anionic/amphoteric surfactant solution is an effective way to induce spontaneous emulsification in the absence of salts or co-solvents.

Key words: spontaneous emulsification, dynamic interfacial tension, interface dilatational elasticity, Marangoni effect

1 INTRODUCTION

In many industrial processes, it is necessary to remove "oily" soil from fabrics and hard surfaces. From an economic and energy point of view, it is important to reduce the time required for this step. Therefore, it is necessary to improve the efficiency of the washing step. One of the goals of this study was to investigate methods for inducing spontaneous emulsification using practical surfactant systems.

The three main mechanisms for soil removal are emulsification, solubilization, and roll-up. In particular, spontaneous emulsification, a process that occurs without any mechanical work\(^1\), is an important interfacial phenomenon that can help to achieve effective detergency. One of the ways to achieve spontaneous emulsification is the temporary appearance of a negative interfacial tension, which induces instability of the interface\(^2\). For example, it has been reported that microemulsions can be generated by mixing long-chain alcohols or fatty acids to oils or by increasing the washing temperature near the phase inversion temperature (PIT)\(^3\). However, most of these systems involve the addition of salts, co-solvents or require heating.

Other approaches to generate low interfacial tensions and enhanced surface activities involve mixed surfactant systems. These systems have superior interfacial or surface properties compared to single surfactants and often exhibit a phenomenon known as synergism. In mixed surfactant systems, synergism is manifested as a lowering in critical micelle concentration (CMC), enhancement in surface activities, improvement in foaming properties, higher clouding point of nonionic surfactants, and lower Krafft point of ionic surfactants\(^4\--^12\). Thus, mixed surfactants are used more widely than single surfactants for industrial applications. In particular, mixed systems comprising anionic and cationic surfactants produce the largest synergistic effects, such as the lowest surface tension and CMC values owing...
to strong interactions between surfactant molecules with oppositely charged head groups\(^{13,14}\). Thus, we tried to induce spontaneous emulsification by using anionic-cationic mixed surfactant solutions, eliminating the need for heating or adding salts or co-solvents.

These anionic-cationic surfactant mixtures, especially their equimolar mixtures, can precipitate easily with increasing concentration or changes in pH\(^{15,16}\). However, the solubility of anionic-cationic mixed systems can be improved by inserting polyoxyethylene moieties into the hydrocarbon chain or hydrophilic group of surfactant molecules\(^{17}\). For example, sodium polyoxyethylene alkyl ether sulfate (AES) is an anionic surfactant with polyoxyethylene groups in the hydrocarbon chain, and therefore, AES can be used to improve the solubility of a mixed surfactant solution\(^{18,19}\). AES is used in fabric detergents, kitchen detergents, body cleansers, shampoo, and many other personal care products\(^{20}\). On the other hand, alkyltrimethyl amine oxide (AO) is an amphoteric surfactant. In aqueous solution, AO exists as a mixture comprising protonated hydroxyl amine (cationic AO) and deprotonated amine oxide (nonionic AO) species; their relative amounts depend on the pH of the aqueous solution\(^{21,22}\). Industrially, AO surfactants are used as foam boosters and for the production of soaps that are mild to the skin\(^{23,24}\).

For these reasons, mixed AES and cationic-nonionic mixed AO surfactant solutions are often used in liquid detergents and shampoos\(^{25}\). Even under neutral conditions, these AES/AO mixtures possess enough solubility to be used in liquid type products\(^{26}\). However, to our knowledge, there has been no study that has assessed the synergistic effects on oil/water interfacial activities. In this paper, we report the spontaneous emulsification of triolein, which is the main component of food oils and human sebum soil, by mixed AES/AO systems, and analyze its dynamic interfacial properties.

### 2 EXPERIMENTAL PROCEDURES

#### 2.1 Materials and Reagents

AES (Shinorin® SPE-1150, \(M_w = 339.7\)) and N, N-dimethyldodecyl amine oxide (DDAO, CADENAX® DM12D-W, \(M_w = 229.4\)) were supplied by New Japan Chemical Co. Ltd. and Lion Specialty Chemicals Co. Ltd., respectively. Triolein and ethyl alcohol were purchased from Kanto Chemical Co. Inc., whereas citric acid and Sudan IV were purchased from Tokyo Chemical Industry Co. Ltd. Anhydrous calcium chloride and NaOH aqueous solution (0.5 M) were purchased from Wako Pure Chemical Industries Ltd. All the materials were used without further purification. The hardness of the water samples was adjusted using anhydrous calcium chloride. Ultra-pure water was used for the preparation of the samples.

#### 2.2 Methods

##### 2.2.1 Preparation of the surfactant mixed solutions

Stock solutions containing mixtures of AES and DDAO at desired molar ratios (totaling 20 wt%) were prepared by dissolving the necessary amounts of the two surfactants in water along with 0.26 wt% of citric acid and 7 wt% of ethyl alcohol. The pH values of the solutions were adjusted to 7.75 using 0.5 M NaOH. The mole fraction of DDAO in the solution \(X_{DDAO}\) may be defined by Eq. 1

\[
X_{DDAO} = \frac{M_{DDAO}}{M_{AES} + M_{DDAO}} \tag{1}
\]

where \(M_{DDAO}\) and \(M_{AES}\) are the mole fractions of DDAO and AES, respectively. The compositions of the stock solutions and the values of CMC (measured by the Wilhelmy plate method using Kruss K100 Surface tensiometer at 25°C) are listed in Table 1. The stock solutions were subsequently diluted in hard water (hardness: 59 mg L\(^{-1}\) as CaCl\(_2\), 3°dH) to the required surfactant concentration.

##### 2.2.2 Detergency tests

The detergency performance of each surfactant solution was evaluated quantitatively by determining the percent-

### Table 1 Composition of the stock solutions.

| \(X_{DDAO}\) | AES/ wt% | DDAO/ wt% | Ethyl alcohol/ wt% | Citric acid/ wt% | CMC/ \(\times 10^{-4}\) wt% |
|------------|----------|-----------|-------------------|-----------------|------------------------|
| 0          | 20.0     | 0.00      | 7.00              | 0.26            | 89.2                   |
| 0.23       | 16.7     | 3.33      | 7.00              | 0.26            | 67.8                   |
| 0.33       | 15.0     | 5.00      | 7.00              | 0.26            | 35.4                   |
| 0.43       | 13.3     | 6.67      | 7.00              | 0.26            | 32.0                   |
| 0.60       | 10.0     | 10.0      | 7.00              | 0.26            | 16.6                   |
| 0.75       | 6.67     | 13.3      | 7.00              | 0.26            | 17.6                   |
| 0.82       | 5.00     | 15.0      | 7.00              | 0.26            | 20.1                   |
| 0.88       | 3.33     | 16.7      | 7.00              | 0.26            | 37.0                   |
| 1          | 0.00     | 20.0      | 7.00              | 0.26            | 81.3                   |

---

*J. Oleo Sci.* 64, (9) 953-962 (2015)
Spontaneous emulsification in the absence of salts or co-solvents

J. Oleo Sci. 64, (9) 953-962 (2015)

2.2.3 Determination of the detergency behavior of surfactant solutions

Detergency behavior was observed using the system illustrated schematically in Fig. 1. PP pieces (50/100 mm) adhered with triolein (0.05 g, containing 0.005 wt% Sudan IV as a stainer) were immersed gently in surfactant solutions (1 wt%, 250 mL) at 25°C. Pictures of oil droplets at 30 s and 3 min after immersion were acquired with CANON EOS 50D.

2.2.4 Evaluation of the equilibrium interfacial tension

Equilibrium interfacial tension ($\gamma_{eq}$) between triolein and surfactant micellar solutions was measured using the spinning drop method with a Spinning Drop Tensiometer-SITE100 (Kurss Co.). Triolein (0.3-0.5 μL) was injected into surfactant solutions (1 wt%) at 25°C (rotation frequency: 5000 rpm).

2.2.5 Evaluation of dynamic interfacial tension

Dynamic interfacial tension ($\gamma(t)$) between triolein and surfactant micellar solutions was measured using the rising drop method with a Drop Volume Tensiometer-DVT-30 (Kurss Co.). Triolein was injected into surfactant solutions (0.01 wt%) at a rate of 100-0.1 μL min⁻¹ at 25°C. The dynamic interfacial tension at a constant surfactant concentration can be represented by the following relaxation function (Eq. 3)²⁷.

$$\gamma = \gamma_{eq} + \frac{\gamma_{eq} - \gamma_{0}}{1 + (t/t^*)^n}$$

where $\gamma_{eq}$ is the equilibrium interfacial tension, obtained by the spinning drop method, $\gamma_0$ is the equilibrium interfacial tension (28.93 mN m⁻¹), determined by the spinning drop method between triolein and the solvent (aqueous solution containing 35 ppm ethyl alcohol and 1.3 ppm citric acid), $t^*$ is the time when $\gamma(t)$ reaches the intermediate value between $\gamma_0$ and $\gamma_{eq}$, and $n$ is a constant. The values of $t^*$ and $n$ are calculated by applying a successive approximation technique to Eq. 3. The differential form of Eq. 3 may be represented by Eq. 4.

$$\frac{d\gamma}{dt} = \frac{n (t/t^*)^{n-1}}{1 + (t/t^*)^n} \frac{1}{\gamma}$$

From Eq. 4, the maximum rate of decrease in interfacial tension ($d\gamma/dt)_{max}$ can be obtained by substituting $t^*$ for $t$, as shown in Eq. 5.

$$(d\gamma/dt)_{max} = -n (\gamma_0 - \gamma_{eq})/4 t^*$$

2.2.6 Evaluation of interfacial dilatational elasticity

The interfacial dilatational elasticity ($E$) was measured using an oscillating rising drop tensiometer Tracker (Teclis Co.). Triolein (2.5-3.5 mL) was injected into the surfactant solution (6 mL, 0.01 wt%) at 25°C. The oscillation period was set at 10 s (0.1 Hz). The method involved automatically controlled sinusoidal interfacial compression and expansion of the oil drop at a desired amplitude and frequency and the determination of the interfacial tension and interfacial area by analyzing the changes in the drop shape from digital images of the drop. The value of $E$, which is also known as Marangoni elasticity, was derived from the change in the interfacial tension resulting from a small change in the interfacial area. The $E$ value obtained 200 s after the start of the dilatations was recorded, to ensure equilibrium interfacial tension. The value of $E$ for an oil/water interface with an area of $A$, which is in periodic dilatation, is defined by Eq. 6.

$$E = \frac{d\gamma}{d\ln A}$$

where $d\gamma$ is the small change in interfacial tension due to a small change in the area $d\ln A$⁻¹.

2.2.7 Evaluation of the zeta potential of the mixed micellar solutions

Zeta potential of the mixed AES/DDAO micellar solutions (1 wt%) was measured with the laser Doppler method using ZETASIZER Nano-ZS (Malvern Co.). All the measurements were conducted at 25°C.

2.2.8 Evaluation of the mole fraction of protonated DDAO

DDAO is an amphoteric surfactant that can exist both in the cationic (C₆H₄N⁺ (CH₃)₃OH) and nonionic (C₁₂H₂₅N⁺ (CH₂)₂O) forms. The mole fraction of protonated DDAO is affected both by the presence of an anionic surfactant as well as the pH of the solution. The protonation equilibrium
in the presence of AES may be represented by Eq. 7:

$$C_{12}H_{25}N(CH_3)_2O + AESNa + H_2O \rightarrow C_{12}H_{25}N^+ (CH_3)_2OH + AES^- + Na^+ + OH^-$$

Eq. 7

To calculate the mole fraction of cationic DDAO at different pH values, the mixed surfactant solution of c-1, 2 was subjected to hydrogen ion titration as follows. The initial mole fraction of cationic DDAO in the solution was estimated by measuring the pH of DDAO solution before and after adding AES solution. The pH of the solution increased after adding the AES solution, indicating the formation of ion pairs between AES and DDAO or protonation of DDAO. However, the estimated mole fraction of cationic DDAO was insignificant. Titration was performed by adding 0.5 M hydrochloric acid solution to 30 mL of the mixed surfactant solution at 25°C. The concentration of cationic DDAO at each pH value was equal to that of the hydroxyl ions ([OH⁻]) generated, as calculated by Eq. 8.

$$[H^+]_{\text{final}} = [H^+]_{\text{initial}} - [OH^-] + [H^+]_{\text{add}}$$

Eq. 8

In this equation, [H⁺]_{final}, [H⁺]_{initial}, and [H⁺]_{add} are the total H⁺ concentration of the solution, initial H⁺ concentration of the solution, and the concentration of the H⁺ added to the solution, respectively.

3 RESULTS AND DISCUSSION

3.1 Detergency of AES/DDAO systems for triolein

Figure 2 shows images of triolein droplets at the interface between PP and a 1 wt% AES/DDAO micellar solution at regular intervals. When the mole fraction of DDAO (X_{DDAO} = 0.60) was subjected to hydrogen ion titration as follows. The initial mole fraction of cationic DDAO in the solution was estimated by measuring the pH of DDAO solution before and after adding AES solution. The pH of the solution increased after adding the AES solution, indicating the formation of ion pairs between AES and DDAO or protonation of DDAO. However, the estimated mole fraction of cationic DDAO was insignificant. Titration was performed by adding 0.5 M hydrochloric acid solution to 30 mL of the mixed surfactant solution at 25°C. The concentration of cationic DDAO at each pH value was equal to that of the hydroxyl ions ([OH⁻]) generated, as calculated by Eq. 8.

$$[H^+]_{\text{final}} = [H^+]_{\text{initial}} - [OH^-] + [H^+]_{\text{add}}$$

Eq. 8

In this equation, [H⁺]_{final}, [H⁺]_{initial}, and [H⁺]_{add} are the total H⁺ concentration of the solution, initial H⁺ concentration of the solution, and the concentration of the H⁺ added to the solution, respectively.

3 RESULTS AND DISCUSSION

3.1 Detergency of AES/DDAO systems for triolein

Figure 2 shows images of triolein droplets at the interface between PP and 1 wt% AES/DDAO micellar solution at regular intervals. When the mole fraction of DDAO (X_{DDAO} = 0.60) was subjected to hydrogen ion titration as follows. The initial mole fraction of cationic DDAO in the solution was estimated by measuring the pH of DDAO solution before and after adding AES solution. The pH of the solution increased after adding the AES solution, indicating the formation of ion pairs between AES and DDAO or protonation of DDAO. However, the estimated mole fraction of cationic DDAO was insignificant. Titration was performed by adding 0.5 M hydrochloric acid solution to 30 mL of the mixed surfactant solution at 25°C. The concentration of cationic DDAO at each pH value was equal to that of the hydroxyl ions ([OH⁻]) generated, as calculated by Eq. 8.

$$[H^+]_{\text{final}} = [H^+]_{\text{initial}} - [OH^-] + [H^+]_{\text{add}}$$

Eq. 8

In this equation, [H⁺]_{final}, [H⁺]_{initial}, and [H⁺]_{add} are the total H⁺ concentration of the solution, initial H⁺ concentration of the solution, and the concentration of the H⁺ added to the solution, respectively.

3 RESULTS AND DISCUSSION

3.1 Detergency of AES/DDAO systems for triolein

Figure 2 shows images of triolein droplets at the interface between PP and 1 wt% AES/DDAO micellar solution at regular intervals. When the mole fraction of DDAO (X_{DDAO} = 0.60) was subjected to hydrogen ion titration as follows. The initial mole fraction of cationic DDAO in the solution was estimated by measuring the pH of DDAO solution before and after adding AES solution. The pH of the solution increased after adding the AES solution, indicating the formation of ion pairs between AES and DDAO or protonation of DDAO. However, the estimated mole fraction of cationic DDAO was insignificant. Titration was performed by adding 0.5 M hydrochloric acid solution to 30 mL of the mixed surfactant solution at 25°C. The concentration of cationic DDAO at each pH value was equal to that of the hydroxyl ions ([OH⁻]) generated, as calculated by Eq. 8.

$$[H^+]_{\text{final}} = [H^+]_{\text{initial}} - [OH^-] + [H^+]_{\text{add}}$$

Eq. 8

In this equation, [H⁺]_{final}, [H⁺]_{initial}, and [H⁺]_{add} are the total H⁺ concentration of the solution, initial H⁺ concentration of the solution, and the concentration of the H⁺ added to the solution, respectively.

3 RESULTS AND DISCUSSION

3.1 Detergency of AES/DDAO systems for triolein

Figure 2 shows images of triolein droplets at the interface between PP and 1 wt% AES/DDAO micellar solution at regular intervals. When the mole fraction of DDAO (X_{DDAO} = 0.60) was subjected to hydrogen ion titration as follows. The initial mole fraction of cationic DDAO in the solution was estimated by measuring the pH of DDAO solution before and after adding AES solution. The pH of the solution increased after adding the AES solution, indicating the formation of ion pairs between AES and DDAO or protonation of DDAO. However, the estimated mole fraction of cationic DDAO was insignificant. Titration was performed by adding 0.5 M hydrochloric acid solution to 30 mL of the mixed surfactant solution at 25°C. The concentration of cationic DDAO at each pH value was equal to that of the hydroxyl ions ([OH⁻]) generated, as calculated by Eq. 8.

$$[H^+]_{\text{final}} = [H^+]_{\text{initial}} - [OH^-] + [H^+]_{\text{add}}$$

Eq. 8

In this equation, [H⁺]_{final}, [H⁺]_{initial}, and [H⁺]_{add} are the total H⁺ concentration of the solution, initial H⁺ concentration of the solution, and the concentration of the H⁺ added to the solution, respectively.

3 RESULTS AND DISCUSSION

3.1 Detergency of AES/DDAO systems for triolein

Figure 2 shows images of triolein droplets at the interface between PP and 1 wt% AES/DDAO micellar solution at regular intervals. When the mole fraction of DDAO (X_{DDAO} = 0.60) was subjected to hydrogen ion titration as follows. The initial mole fraction of cationic DDAO in the solution was estimated by measuring the pH of DDAO solution before and after adding AES solution. The pH of the solution increased after adding the AES solution, indicating the formation of ion pairs between AES and DDAO or protonation of DDAO. However, the estimated mole fraction of cationic DDAO was insignificant. Titration was performed by adding 0.5 M hydrochloric acid solution to 30 mL of the mixed surfactant solution at 25°C. The concentration of cationic DDAO at each pH value was equal to that of the hydroxyl ions ([OH⁻]) generated, as calculated by Eq. 8.

$$[H^+]_{\text{final}} = [H^+]_{\text{initial}} - [OH^-] + [H^+]_{\text{add}}$$

Eq. 8

In this equation, [H⁺]_{final}, [H⁺]_{initial}, and [H⁺]_{add} are the total H⁺ concentration of the solution, initial H⁺ concentration of the solution, and the concentration of the H⁺ added to the solution, respectively.
more than 0.60, the detergency decreases, with almost no emulsification being observed in the DDAO-only solution (X_{DDAO} = 1).

3.2 Equilibrium interfacial tension for triolein

Figure 4 shows the equilibrium interfacial tension values, $\gamma_{eq}$, as a function of $X_{DDAO}$ for triolein–1 wt% AES/DDAO micellar solutions. The values of $\gamma_{eq}$ for the mixed AES/DDAO system are lower than those for the individual surfactants. However, the values of $\gamma_{eq}$ are similar for solutions with $X_{DDAO}$ values between 0.2 and 0.8. Given this result and that the maximum detergency was obtained at $X_{DDAO}$ values of 0.60 (see Fig. 3), we believe that there are other factors at play in the removal of oil in these systems.

Next, we focused on the dilatational behavior and measured the rate of decrease of interfacial tension for triolein in AES/DDAO systems. Furthermore, the resistance to dilatation of the oil/water interface was evaluated as a measure of the interface dilatational elasticity for triolein in AES/DDAO systems similar to the method by Tadros.

3.3 Dynamic interfacial tension for triolein

Figure 5 shows the dynamic interfacial tension, $\gamma_t$, values of triolein–0.01 wt% AES/DDAO micellar solutions. In 1 wt% AES/DDAO micellar solutions, we could not determine the $\gamma_t$ values because these values were too low to have a drop shape, which is required for determining the $\gamma_t$ values by the rising drop method. Therefore, we decided to measure the $\gamma_t$ values in a 0.01 wt% micellar solution. The solid lines shown in the figure were calculated using Eq. 3.

For every mole fraction, the values of $\gamma_t$ decreased with increasing surface age. The values of $\gamma_t$ decrease with increasing values of $X_{DDAO}$, reach a minimum at $X_{DDAO} = 0.60$, and then increase for $X_{DDAO}$ values greater than 0.60. In the case of $X_{DDAO} = 0$, lower interfacial tension was observed at shorter surface age values, but the rate of decrease of interfacial tension was slower than that for $X_{DDAO}$ values between 0.23 and 0.88. This result suggests that the negative charge of the AES adsorbed at the oil/water interface inhibits additional adsorption at the interface. We describe this effect in section 3.5. In the case of $X_{DDAO} = 1$, the highest value of $\gamma_t$ was observed because, at the oil/water interface, nonionic DDAO is more soluble in the oil phase than AES.

The values of the parameters we used to calculate $(d\gamma_t/dt)_{max}$ are listed in Table 2. The values of $t^*$, which is the...
time when $\gamma_t$ attains values intermediate between $\gamma_0$ and $\gamma_{eq}$ decrease with increasing values of $X_{DDAO}$ and reach a minimum at $X_{DDAO} = 0.60$. For values of $X_{DDAO}$ greater than 0.60, the values of $t^*$ increase. The values of $n$, which is related to the slope of the linear region of the dynamic interfacial tension curve, increases with increasing $X_{DDAO}$ values, reach a maximum at $X_{DDAO} = 0.60$, and decrease for $X_{DDAO}$ values greater than 0.60. The values of $\frac{d\gamma_t}{dt}_{max}$, which corresponds to the maximum rate of decrease in $\gamma_t$, increase with increasing values of $X_{DDAO}$, reach a maximum at $X_{DDAO} = 0.60$, and decrease for values of $X_{DDAO}$ beyond 0.60 in Fig. 6.

Figure 7 shows the $(d\gamma_t/dt)_{max}$ values as a function of total surfactant concentration. Over the entire range of surfactant concentrations tested (0.0001 to 0.01 wt%), the $(d\gamma_t/dt)_{max}$ values of the $X_{DDAO} = 0.60$ solution are larger than those of the $X_{DDAO} = 0$ and $X_{DDAO} = 1$ solutions. Furthermore, over the entire range of surfactant concentrations tested (0.0001 to 1 wt%), no phase formations, which lead to a discontinuous change in the $(d\gamma_t/dt)_{max}$ values, were observed. Therefore, it is likely that the $(d\gamma_t/dt)_{max}$ values of the $X_{DDAO} = 0.60$ solution is the largest among these mole fractions of AES/DDAO mixed solutions even at 1 wt% of the surfactant.

The $(d\gamma_t/dt)_{max}$ corresponds to the rate of adsorption at the oil/water interface. Therefore, in subsequent sections, we discuss the effect of $(d\gamma_t/dt)_{max}$ values on the interfacial elasticity for inducing spontaneous emulsification.

### 3.4 Interface dilatational elasticity for triolein

Figure 8 shows the dependence of $E$ on $X_{DDAO}$ values in 0.01 wt% AES/DDAO micellar solutions. The values of $E$ decrease with increase in $X_{DDAO}$ reach a minimum at $X_{DDAO} = 0.60$, and increase for $X_{DDAO}$ values greater than 0.60. Consequently, the oil/water interface of the $X_{DDAO} = 0.60$ solution is the most easily expanded.

Figure 9 shows the relation between $E$ and $(d\gamma_t/dt)_{max}$. $E$ values decrease with increasing $(d\gamma_t/dt)_{max}$ values with a correlation factor $R^2 = 0.886$. It is well known that $E$ mainly depends on the kinetics of the surfactant molecules

| $X_{DDAO}$ | $\gamma_{eq}$/mN·m$^{-1}$ | $t^*/s$ | $n$ | $(d\gamma_t/dt)_{max}$/mN·m$^{-1}$·s$^{-1}$ |
|------------|-----------------|--------|-----|------------------------|
| 0          | 0.251           | 7.9    | 1.15| 0.99                   |
| 0.23       | 0.241           | 6.4    | 2.10| 2.2                    |
| 0.33       | 0.253           | 5.8    | 2.40| 2.8                    |
| 0.43       | 0.301           | 5.6    | 2.60| 3.2                    |
| 0.60       | 0.318           | 5.1    | 2.70| 3.6                    |
| 0.75       | 0.245           | 5.2    | 1.99| 2.7                    |
| 0.82       | 0.220           | 5.8    | 1.80| 2.2                    |
| 0.88       | 0.225           | 6.5    | 1.60| 1.7                    |
| 1          | 0.557           | 289.5  | 0.60| 0.020                  |

Fig. 6 Calculated value of $(d\gamma_t/dt)_{max}$ for the triolein–0.01 wt% AES/DDAO micellar solutions at 25°C.

Fig. 7 Dependence of $(d\gamma_t/dt)_{max}$ on the AES/DDAO concentration at 25°C.
Spontaneous emulsification in the absence of salts or co-solvents

between the bulk solution and interface (i.e., the Marangoni effect\textsuperscript{28, 30, 31}) and this effect supports this result. These results confirm that $E$ values can be decreased by increasing $(d\gamma/dt)_{\text{max}}$ values, and then the oil/water interface is easily expanded. In other words, the Marangoni effect is suppressed.

Figure 10 shows a schematic representation of the spontaneous and nonspontaneous emulsification processes at the interface between a PP surface and 1 wt\% AES/DDAO micellar solutions. It is well known that the Marangoni effect leads to contraction or expansion of the oil/water interface\textsuperscript{28, 31}; however, there are no previous reports of spontaneous emulsification being induced by suppression of the Marangoni effect, as shown in Fig. 10a. Based on our results on the rate of decrease in interfacial tension and interface dilatational elasticity, we conclude that the most rapid spontaneous emulsification (see Fig. 2c) and

![Graph](image1)

Fig. 8 Dependence of interface dilatational elasticity on $X_{\text{DDAO}}$ in 0.01 wt\% AES/DDAO micellar solutions at 25°C.

![Graph](image2)

Fig. 9 Relationship between $E$ and $(d\gamma/dt)_{\text{max}}$. The points labeled in the figure correspond to various $X_{\text{DDAO}}$ values. a: $X_{\text{DDAO}} = 0$, b: $X_{\text{DDAO}} = 0.33$, c: $X_{\text{DDAO}} = 0.60$, and d: $X_{\text{DDAO}} = 1$.

![Diagram](image3)

Fig. 10 Schematic representation of spontaneous emulsification at the interface between the surface of PP and 1 wt\% AES/DDAO micellar solutions, (a) $X_{\text{DDAO}} = 0.60$, (b) $X_{\text{DDAO}} = 0, 1$. 

\textit{J. Oleo Sci.} 64, (9) 953-962 (2015)
maximum detergency (see Fig. 3), in the absence of salts or co-solvents, are obtained at the maximum suppression of the Marangoni effect ($X_{DDAO} = 0.60$), as shown in Figs. 6 and 8. On the other hand, in single surfactant solutions of AES and DDAO, which have smaller $(dy/dt)_{max}$ values than those of the mixed surfactant solutions, spontaneous emulsification is not induced (Fig. 10b).

To understand why $(dy/dt)_{max}$ and $E$ values were the maximum and minimum, respectively, at $X_{DDAO} = 0.60$, we proposed a hypothesis based on the following previous reports. Chen, Miller, and Garrett proposed that the solubilization efficiency of triolein was increased by the decreasing electrostatic (double layer) repulsion between the micelles and the oil/water interface. Based on these reports, we hypothesized that the dilatational elasticity decreases with increasing number of micelles near the drop surface owing to a decrease in the electrostatic repulsion between the micelles and the drop surface. To verify this hypothesis, we described the micelle behaviors in the next section.

3.5 Effect of a micelle approaching the oil/water interface on the dilatational elasticity

3.5.1 DDAO molar ratio dependence of the zeta potential of micelles on $E$

Figure 11 shows the $X_{DDAO}$ dependence of the zeta potential of the micellar surface in 1 wt% AES/DDAO solutions at 25°C. With increasing $X_{DDAO}$ values between 0 and 0.6, the zeta potential of the micellar surface increases and approaches 0 mV. This result indicates that the negative charge of micelles was neutralized by cationic DDAO, and the electrostatic repulsion between the micelles and the oil/water interface decreased with increasing $X_{DDAO}$ values. In this region, the interfacial dilatational elasticity decreases with increasing $X_{DDAO}$ values (see Fig. 7), and these results support our hypothesis.

On the other hand, the zeta potential of the micellar surface did not change with increasing $X_{DDAO}$ values between 0.6 and 1. We, unfortunately, cannot provide a satisfactory explanation for this result. We are currently investigating the cause of this result on the assumption that the dilatational elasticity increases with decreasing dynamic interfacial tension as a result of the high solubility of DDAO into the oil phase from the oil/water interface.

To verify our hypothesis further, we evaluated the values of $E$ as a function of electrostatic repulsion induced by varying the pH and adding counterions.

3.5.2 pH dependence of micelle charges on $E$

The relationship between the pH of the solution and the composition ratio of nonionic DDAO and cationic DDAO at $X_{DDAO} = 0.60$ is shown in Fig. 12. DDAO mainly exists as a cationic surfactant in a solution at low pH (less than 6.4) and precipitation is caused by formation of AES/DDAO ion-pairs. At neutral pH, both cationic and nonionic DDAO species exist and form a mixed micellar solution. At high pH (larger than 9.1), DDAO mainly exists as a nonionic surfactant and forms mixed micellar solutions.

Figure 13 shows the effect of pH on $E$ in the $X_{DDAO} = 0.60$ solution. Under acidic conditions (pH less than 6.4), $E$ increases from 1.2 to 13.9 mN·m$^{-1}$ with decreasing pH values and increasing precipitation of AES/DDAO ion-pair complexes. With increase in precipitation, the amount of surfactant molecules adsorbed at the oil/water interface decreases, leading to increased $E$ values. Under alkaline conditions (pH larger than 8.0), $E$ increases from 2.0 to 3.5 mN·m$^{-1}$ with increasing pH values. Therefore, under alkaline conditions, we find that $E$ values increase due to the increase in the negative charge of the micelles with de-
creasing cationic DDAO ratio. At neutral conditions (around pH 7.0), we observed the minimum value of $E$ (1.2 mN·m⁻¹). Therefore, we find that under neutral conditions, $E$ assumes minimum value, since the negative charge on the micelles decreases with increasing cationic DDAO ratio. These results confirm that the $E$ values can be decreased by increasing the number of micelles near the oil drop surface, since increasing the number of micelles results from a decrease in the electrostatic repulsion between the micelles and the drop surface. These results provide considerable support for our hypothesis.

3.5.3 Calcium ion concentration dependence of micelle charges on $E$

Table 3 shows the calcium ion concentration dependence of zeta potentials of micelles, $\gamma_{eq} (d\gamma_t/dt)_{max}$ of a triolein-water interface, and $E$ values in AES ($X_{DDAO} = 0$) micellar solutions at 25°C. With increasing Ca²⁺ concentration, the zeta potential of the micellar surface approaches 0 mV, making the micelles more accessible to the oil/water interface. Moreover, the $\gamma_{eq}$ values hardly change and the $E$ values decrease with increasing in $(d\gamma_t/dt)_{max}$. These results support our hypothesis.

| Ca²⁺ /mM | Zeta potential /mV | $\gamma_{eq}$ /mN·m⁻¹ | $(d\gamma_t/dt)_{max}$ /mN·m⁻¹·s⁻¹ | $E^0$ /mN·m⁻¹ |
|---|---|---|---|---|
| 0.00 | -55.9 | 0.203 | 0.0040 | 13.8 |
| 0.09 | -55.7 | 0.184 | 0.62 | 12.7 |
| 0.18 | -49.5 | 0.182 | 0.88 | 6.2 |
| 0.54 | -36.0 | 0.175 | 0.99 | 2.4 |
| 0.89 | -24.7 | 0.176 | 1.8 | 2.1 |

$a$ Total concentration of the surfactant solution is 0.01 wt%. $b$ Total concentration of the surfactant solution is 1 wt%.

4 CONCLUSION

We studied the dynamic emulsification process of triolein in AES/DDAO mixed micellar solutions using dynamic interfacial tension and elasticity measurements. Through these characterizations, spontaneous emulsification could be induced owing to the increased rate of decrease in dynamic interfacial tension at equimolar ratios of AES/DDAO. We clarified that the increase in the rate of decrease in dynamic interfacial tension tends to decrease the interfacial elasticity, by increasing number of micelles near oil drop surface with decrease in the electrostatic repulsion between the micelles and the drop surface. Moreover, it was confirmed that the low interfacial elasticity allows for much greater suppression of the Marangoni effect and generates spontaneous emulsification.

In our study, we demonstrate that controlling the molar ratio of a mixed anionic/amphoteric surfactant solution is an effective way to induce spontaneous emulsification in the absence of salts or co-solvents.

References
1) Davies, J. T.; Rideal, E. K. Disperse systems and adhesion in Interfacial phenomena 2nd Edition, Academic press, New York, pp. 360-367 (1963).
2) Ogino, K.; Ota, M. Studies of spontaneous emulsification. II. The effect of nonionic surfactants. Bull. Chem. Soc. Jpn. 49, 1187-1190 (1976).
3) Miller, C. A.; Raney, K. H. Solubilization-emulsification mechanisms of detergency. Colloids Surfaces A: Physicochem. Eng. Aspects 74, 169-215 (1993).
4) Rosen, M. J.; Hua, X. Y. Synergism in binary mixtures of surfactants: II. Some experimental data. J. Am. Oil Chem. Soc. 59, 582-585 (1982).
5) Abe, M.; Kato, K.; Ogino. K. Effects of inorganic electrolytes and of pH on micelle formation of amphoteric-anionic mixed surfactant systems. J. Colloid Interface Sci. 127, 328-335 (1989).
6) Valaulikar, B. S.; Manohar, C. The mechanism of clouding in Triton X-100: The effect of additives. J. Colloid Interface Sci. 108, 403-406 (1985).

Table 3 Dependence of the zeta potential, $\gamma_{eq}$, $(d\gamma_t/dt)_{max}$, and $E$ values on the Ca²⁺ concentration in AES ($X_{DDAO} = 0$) micellar solutions at 25°C.
7) Shiloach, A.; Blankschtein, D. Prediction of critical micelle concentrations and synergism of binary surfactant mixtures containing zwitterionic surfactants. *Langmuir* **13**, 3968-3981 (1997).

8) Mulqueen, M.; Blankschtein, D. Prediction of equilibrium surface tension and surface adsorption of aqueous surfactant mixtures containing zwitterionic surfactants. *Langmuir* **16**, 7640-7654 (2000).

9) Iwasaki, T.; Ogawa, M.; Esami, K.; Meguro, K. Interactions between betaine-type zwitterionic and anionic surfactants in mixed micelles. *Langmuir* **7**, 30-35 (1991).

10) Christov, N. C.; Denkov, N. D.; Kralchevsky, P. A.; Anthapadmanabhan, K. P.; Lips, A. Synergistic sphere-to-rod micelle transition in mixed solutions of sodium dodecyl sulfate and cocoamidopropyl betaine. *Langmuir* **20**, 565-571 (2004).

11) Kume, G.; Gallotti, M.; Nunes, G. Review on anionic/cationic surfactant mixtures. *J. Surfact. Deterg.* **11**, 1-11 (2008).

12) Wang, R.; Li, Y.; Li, Y. Interaction between cationic and anionic surfactants: detergency and foaming properties of mixed systems. *J. Surfact. Deterg.* **17**, 881-888 (2014).

13) Matsuki, H.; Aratono, M.; Kaneshina, S.; Motomura, K. Extremely strong interaction of sodium decyl sulfate and decyltrimethylammonium bromide in molecular aggregates. *J. Colloid Interface Sci.* **191**, 120-130 (1997).

14) Sohrabi, B.; Gharibi, H.; Tajik, B.; Javadian, S.; Hasheminzadeh, M. Molecular interactions of cationic and anionic surfactants in mixed monolayers and aggregates. *J. phys. Chem. B* **112**, 14869-14876 (2008).

15) Amante, J. C.; Scamehorn, J. F.; Harwell, J. H. Precipitation of mixtures of anionic and cationic surfactants: II. Effect of surfactant structure, temperature, and pH. *J. Colloid Interface Sci.* **144**, 243-253 (1991).

16) Nan, Y.; Liu, H.; Hu, Y. Interfacial tension in phase-separated aqueous cationic/anionic surfactant mixtures. *J. Colloid Interface Sci.* **293**, 464-474 (2006).

17) Cui, Z. G.; Canselier, J. P. Interfacial and micellar properties of some anionic/cationic binary surfactant systems. 1. Surface properties and prediction of surface tension. *Colloid Polym. Sci.* **278**, 22-29 (2000).

18) Alargova, R. G.; Danov, K. D.; Petkov, J. T.; Kralchevsky, P. A.; Broze, G.; Mehreteab, A. Sphere-to-rod transition in the shape of anionic surfactant micelles determined by surface tension measurements. *Langmuir* **13**, 5544-5551 (1997).

19) Parekh, P.; Varade, D.; Parikh, J.; Bahadur, P. Anionic-cationic mixed surfactant systems: Micellar interaction of sodium dodecyl trioxymethylene sulfate with cationic gemini surfactants. *Colloids Surf. A* **385**, 111-120 (2011).

20) Ohbu, K.; Johna, N.; Kashiwa, I. *U. S. Pat.*, 045 134 (1980).

21) Soonravanich, S.; Walsh, S.; Scamehorn, J. F.; Harwell, J. H.; Sabatini, D. A. Interaction between an anionic and an amphoteric surfactant. Part II: Precipitation. *J. Surfact. Deterg.* **12**, 145-154 (2009).

22) Yamashita, Y.; Hoffmann, H.; Maeda, H.; Li, L.; Ballauff, M. Aggregation and phase behavior of a double-chain surfactant, N-dodecyl-N-octyl-N-methylamine oxide, as a function of the protonation degree. *Langmuir* **23**, 1073-1080 (2007).

23) Zhang, H.; Miller, C. A.; Garrett, P. R.; Raney, K. H. Lauryl alcohol and amine oxide as foam stabilizers in the presence of hardness and oily soil. *J. Surfact. Deterg.* **8**, 99-107 (2005).

24) Singh, S. K.; Bajpai, M.; Tyagi, V. K. Amine oxides: A review. *J. Oleo Sci.* **55**, 99-119 (2006).

25) Blanca, N. L.; Carmen, M. P. G.; Maria, J. B. O.; Hiroshi, A. WO, 141 067 (2007).

26) Nishida, K.; Okamoto, Y. *Jpn. Pat.*, 153 956 (2007).

27) Rosen, M. J. Dynamic surface tension of aqueous surfactant solutions: IV relationship to foaming. in *Surfactants in solution*, (K. L. Mittal, ed.) Vol. 11, Plenum Press, New York, pp. 315-327 (1991).

28) Hansen, F. K. Surface dilational elasticity of poly(oxyethylene)-based surfactants by oscillation and relaxation measurements of sessile bubbles. *Langmuir* **24**, 189-197 (2008).

29) Tadros, T. F. Emulsion formation, stability, and rheology. in *Emulsion Formation and Stability*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 1-75 (2013).

30) Shrestha, L. K.; Matsumoto, Y.; Ihara K.; Aramaki, K. Dynamic surface tension and surface dilatational elasticity properties of mixed surfactant/protein systems. *J. Oleo Sci.* **57**, 485-494 (2008).

31) Rosen, M. J. Foaming and antifoaming by aqueous solutions of surfactants. in *Surfactants and Interfacial Phenomena 3rd Edition*, Wiley-Interscience, New York, pp. 277-282 (2004).

32) Chen, B. H.; Miller, C. A.; Garrett, P. R. Rate of solubilization of triolein into nonionic surfactant solutions, *Colloids Surfaces A: Physicochem. Eng. Aspects* **128**, 129-143 (1997).

33) Todorov, P. D.; Marinov, G. S.; Kralchevsky, P. A.; Denkov, N. D.; Durbut, P.; Broze, G.; Mehreteab, A. Kinetics of triglyceride solubilization by micellar solutions of nonionic surfactant and triblock copolymer. 3. Experiments with single drops. *Langmuir* **18**, 7896-7905 (2002).