Formation and Cleansing Performance of Bicontinuous Microemulsions in Water/Poly(oxyethylene) Alkyl Ether/Ester-Type Oil Systems

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Abstract: Phase behaviors in water/poly(oxyethylene) dodecyl ether (C₁₂EOₙ, n = 4, 6, 8)/cetyl isoctanoate (CIO) systems were studied. In the C₁₂EO₄ and C₁₂EO₆ systems, self-assembled structures with positive curvatures, such as O/W microemulsions, and micellar cubic and hexagonal phases, were observed. A wider region of a lamellar liquid-crystalline phase, which included a narrow microemulsion region joined by a miscibility gap, was observed in the C₁₂EO₈ system. The structure of the microemulsion phase in the C₁₂EO₄ system was characterized by pulsed-field-gradient NMR (PFG-NMR) and small angle X-ray scattering (SAXS) techniques. PFG-NMR measurements indicated that the structure of the microemulsion was bicontinuous; both water and oil phases were continuous within the microemulsion. Pair-distance distribution function, p(r), and structure factors obtained by Generalized Indirect Fourier Transformation (GIFT) analysis of the SAXS data showed that the microemulsion domain sizes decreased with an increase in the oil content. The structure of the bicontinuous microemulsion was consistent with the results of a detergency test, in which the microemulsion samples were applied to lipstick dirt on an artificial skin plate. Detergency was observed to be better for the microemulsion at lower oil contents because of the larger oil domain size at these low concentrations.

Key words: bicontinuous microemulsion, ester-type oil, cleansing performance, structure-performance relationship

1 Introduction

Microemulsions are thermodynamically stable isotropic solutions containing water, oil, and a surfactant. The structures of microemulsions are classified into three types as follows: oil-in-water (O/W), water-in-oil (W/O), and bicontinuous. Bicontinuous microemulsions (BMEs) have continuous oil and water phases and show ultralow interfacial tension and maximum solubilization capacity. Therefore, BMEs are suitable candidates for use in tertiary oil recovery and as high performance detergent agents.

BMEs are composed of water and oil domains, which have a length of the order of several tens of nm, and a surfactant monolayer with zero overall curvature. Therefore, BMEs often convert to lamellar liquid crystals with an overall zero curvature as the rigidity of the surfactant layer increases. Typical systems used to formulate the BME are ternary water/poly(oxyethylene)-type surfactant/oil systems. As temperature greatly influences the polarity of a poly(oxyethylene) chain through the large conformational change, ternary water/poly(oxyethylene)-type surfactant/oil systems can be transformed into any type of microemulsion by just changing the temperature. The O/W type is present at low temperature and the W/O type appears at high temperatures. The BME is present at intermediate temperatures. The HLB temperature or the phase inversion temperature, at which the bicontinuous microemulsion exists, is the temperature at which the surfactant layer curvature inverts from positive to negative and the macroemulsion type converts from O/W to W/O.

There are several reports, which have investigated the
application of BMEs for use in the removal of soil or dirt from substrates. Detergent efficiency for the removal of oily dirt from substrates using a microemulsion system is maximized at the HLB temperature of a water/poly(oxyethylene)/alkyl ether/oil system. Removal of liquid paraffin oil from porous polyethylene films was attempted using microemulsions. It was found that removal efficiency depended on the microemulsion type, and BMEs show better efficiency than do the O/W type. Watanabe et al. reported that the BME with silicone oil showed high performance as a make-up remover having both reasonable usability and detergency.

In this paper, we report the formulation and characterization of BMEs in a water/poly(oxyethylene)/alkyl ether/ester-type oil system. Results are confirmed by phase study, pulsed-field-gradient NMR (PFG-NMR), and small angle X-ray scattering (SAXS). The solubilization behavior of ester-type oils is similar to that of aliphatic hydrocarbons. Consequently, systems consisting of water, a poly(oxyethylene)-type surfactant, and an ester-type oil will have an HLB transition temperature. Cetyl isooctanoate (CIO), which is often used for cosmetic products, was used as the ester-type oil in this study. We tested the cleansing performance of the BME with CIO against lipstick dirt on an artificial skin plate.

2 Materials and Methods

2.1 Materials

Homogeneous poly(oxyethylene)dodecyl ethers (C\text{12}EO\text{n}, \text{n} = 4, 6, 8) of product codes BL-4SY, BL-6SY and BL-8SY, respectively, were purchased from Nikko Chemicals, Japan. Cetyl isooctanoate (CIO) was purchased from Nikko Chemicals. Millipore-filtered water was used to prepare all samples.

2.2 Methods

2.2.1 Determination of phase diagrams

Predetermined weights of surfactant, water, and oil were placed in screw-capped glass test tubes and mixed using a vortex mixer. After mixing, the samples were stored water bath at a constant temperature. Phase states were observed by visual inspection using cross-polarized plates.

2.2.2 Small-angle X-ray scattering (SAXS)

Small angle X-ray scattering (SAXS) experiments were performed using a Kratky-type camera (SAXSsess, Anton Paar, Austria) equipped with a PW3830 laboratory X-ray generator (Philips, Netherland) fitted with a long fine-focus sealed-glass X-ray tube (Cu-Kα wavelength = 0.1542 nm). The apparatus was operated at 40 kV, 50 mA. Samples were placed in a custom-designed quartz capillary (1 mm thick) and irradiated for 30 min. SAXS data were evaluated using the generalized indirect Fourier transformation (GIFT) method. The structure of the microemulsion was then determined in real space from the pair-distance distribution function, \(p(r)\). Note that the shape of the \(p(r)\) curve is related to the shape of colloidal particle, and the value of \(r\) at which \(p(r)\) reaches to zero in the higher- \(r\) regime determines the maximum dimension of the colloidal particles. A detailed theoretical description of the GIFT method can be found elsewhere.

2.2.3 Pulsed field gradient NMR (PFG-NMR)

Self-diffusion coefficients of water and oil molecules in microemulsion samples were measured with a Fourier-transformed pulsed-gradient spin-echo technique monitoring the proton NMR spectra. The instrument used was a JNM LA-400 (JEOL, Japan) spectrometer. The peak intensity, which is affected by the diffusion of measured molecules, declined with increasing width of the field gradient pulses during PFG-NMR measurements. The relationship between the attenuation behavior of peak intensity, the self-diffusion coefficient \(D\), and the various parameters of the field gradient is indicated according to the following equation.

\[
\ln\left(\frac{A(\delta)}{A(0)}\right) = -kD\left(\gamma g\delta(4\Delta - \delta)\right)
\]

where \(A(\delta)\) and \(A(0)\) are the peak intensities in the absence and presence of a magnetic field, respectively; \(\gamma\) is the gyromagnetic ratio; \(g\) is the intensity of the field gradient; and \(A\) is the diffusion time, which was set at 50 ms in this study. The self-diffusion coefficient is given by the slope of the line obtained using Eq. (1) by plotting the natural log of the intensity ratio as a function of \(k\).

2.2.4 Detergency Test

A red-colored lipstick (Shiseido, Japan) composed of a mixture containing approximately 85 – 95% oil/wax and 5 – 15% pigments was rubbed on a white-colored artificial skin plate made from a urethane elastomer (BIOSKIN P001-001, Beaulax, Japan). 3.0 mg of the lipstick was applied to the surface of the skin plate in a circular area (d = 10 mm). 0.1 g of a microemulsion sample was then applied directly onto the applied lipstick and was left undisturbed for 5 min. The microemulsion was then washed away using tap water and the artificial skin plate was allowed to dry at room temperature. Color phases (\(a^*\), \(b^*\)) and brightness (\(L^*\)) were measured three times for each sample using a color-difference meter (CR-400, Konica Minolta Sensing, Japan). A color difference value \((\Delta E^*)\) was obtained from the color phase and brightness measurements made on the red-colored part of the artificial skin plate before and after washing. \(\Delta E^*\) was calculated using the following equation:

\[
\Delta E^* = \left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2
\]
3 Results and Discussion

3.1 Phase behavior in water/C_{12}EO_{n}/CIO systems

Figure 1 shows the ternary phase diagrams of the water/C_{12}EO_{n}/CIO systems at 25°C. In the most hydrophilic surfactant, the C_{12}EO_{8} system, micellar ($W_m$), hexagonal ($H_1$), and bicontinuous cubic ($V_1$) phases appear on the water-surfactant axis. When the CIO is added to the aqueous C_{12}EO_{8} system, the $W_m$ phase solubilizes CIO and microemulsions are formed. The solubilization limit of the microemulsions is dependent on the surfactant concentration. Above the solubilization limit, the microemulsion is in equilibrium with an excess oil phase, suggesting that the microemulsion structure must be of the O/W type. At around 40 to 50 wt% of surfactant in water, adding oil induces the formation of the micellar cubic phase ($I_1$), suggesting that CIO is mainly solubilized in the core of micelles. Such oil-induced cubic phase formation is known to occur in several surfactant systems. In the C_{12}EO_{8} system, the $I_1$ phase region is shifted toward the higher oil content region in comparison to the C_{12}EO_{8} system. As the C_{12}EO_{8} is less hydrophilic than the C_{12}EO_{8}, the former will have a smaller spontaneous curvature than the latter. The C_{12}EO_{4} system exhibits a completely different phase behavior compared to the other two systems. For the C_{12}EO_{4} system, the $W_m$, $I_1$, $H_1$, and $V_1$ phases disappear and the $L_α$ phase region expands dramatically in comparison to its expansion in the C_{12}EO_{8} system. The microemulsion ($D$) region is separated from the water-surfactant axis and expands into the higher oil content region. The phase behavior is affected by the molecular weight and the polarity of oil molecules owing to different solubilization sites in micelles or liquid crystals.

Kunieda et al. reported that the phase diagram of water/C_{12}EO_{8}/sarcosine lauroyl isopropyl (SLIP) is completely different from the phase behavior exhibited by water/C_{12}EO_{8}/

![Figure 1](image-url)
aliphatic hydrocarbon oils. However, systems with isopropyl myristate (IPM) exhibit a phase behavior similar to that of aliphatic hydrocarbon oil systems. The present system containing C10E4 oil exhibits a phase behavior similar to that of ternary water/nonionic surfactant/aliphatic hydrocarbons oil systems.

3.2 Microemulsion characterization formed in the water/ C10E4/C10O system

3.2.1 PFG-NMR

There are three types of microemulsion structures, the oil-in-water, the water-in-oil, and the bicontinuous. The PFG-NMR method is a powerful tool used to determine microemulsion structures. We made PFG-NMR measurements of two samples of the C10E4 system in the narrow D phase region. To determine the continuity of both water and oil domains, the self-diffusion constants of both water and oil molecules were measured simultaneously. The obtained self-diffusion constants (D) were divided by the self-diffusion constant of the pure solvent (D0) to obtain a relative self-diffusion constant D/D0. D/D0 ratio values of 1 and 0 indicate complete continuity and complete isolation, respectively. For a bicontinuous structure, D/D0 values for both water and oil have a value of approximately 0.5. The results of the present study are shown in Table 1. The subscripts W and O indicate the values for water and oil molecules, respectively. For the sample with W0 = 0.5, the continuity of the oil phase is slightly higher than that of the water, whereas the opposite result is obtained for the sample with W0 = 0.4. Although there are small differences in the continuities of the two species in both the samples, the results listed in Table 1 indicate that the microemulsions in the D region have a bicontinuous structure.

3.2.2 SAXS

The water and oil domains of microemulsions are several tens of nanometers in length. Therefore, small-angle scattering of X-rays and neutrons (SAXS or SANS) are useful tools for structural characterization of microemulsions.

Figure 2 shows SAXS spectra for the microemulsion samples at W0 = 0.2, 0.3, 0.4, and 0.5. The symbols used represent the scattering intensities in absolute units. The solid and broken lines represent the GIFT fit and the calculated total form factor, nP(q), respectively. All the scattering curves show large deviations from the form factors at the innermost position, suggesting strong interactions between the microdomains of water and oil. The local maxima of the scattering curves in the low-q range are typical of those observed for BME. The position of the low-q peak, which determines the size of oil and water domains, shifts to higher-q as the oil content in the microemulsions increases, which indicates that increasing W0 results in a decrease in the domain size.

Table 1 Relative self-diffusion constants for water (Dw/Dw0) and C10O (Do/Do0) molecules.

<table>
<thead>
<tr>
<th>Composition</th>
<th>W0 = 0.4</th>
<th>W0 = 0.5</th>
</tr>
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<tbody>
<tr>
<td>Dw/Dw0</td>
<td>0.47</td>
<td>0.51</td>
</tr>
<tr>
<td>Do/Do0</td>
<td>0.39</td>
<td>0.66</td>
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Figure 3 shows the real space pair-distance distribution functions (PDDFs), p(r), obtained from the GIFT evaluation of the SAXS data. All the p(r) functions are almost asymmetrical in shape, suggesting that all of the water and oil domains are randomly oriented. We noted that maximum size of the microemulsion domain, Dmax, increased with decreasing W0; Dmax increased from ca. 13 to 26 nm upon decreasing W0 from 0.5 to 0.2. Moreover, the position of the maximum of p(r) in the lower-r side, which semi-quantitatively determines the size of the microemulsion domains, increases with decreasing W0, i.e., the microemulsion domain swells with increasing oil content.

Figure 4 presents a master plot of p(r)/p(rmax) vs. r/rmax, which shows that all curves for these systems almost overlap each other on the lower r/rmax side of the curves, while exhibiting only small deviations on the higher r/rmax side. These features in the master plot demonstrate that changing the oil content in the system causes only minor changes (small fluctuations) in the shape of the microemulsion domains, i.e. oil content does not induce a substantial modification in the microemulsion domains although size changes are significant.
Figure 5 shows the static structure factor, $S(q)$, curves at different oil contents. Oscillations in the $S(q)$ curves in the lower-$q$ side indicate strong interactions between the water and the oil domains. We noted that the $S(q)$ peak position shifted to higher-$q$ for higher $W_o$, suggesting a smaller domain size for higher oil content, which is in a good agreement with the results for these systems that were deduced from the pair-distance distribution function (Fig. 3).

3.3 Cleansing performance of BME

Table 2 shows the results of color difference values ($\Delta E^*$) for the artificial skin plates after they were washed with the BME samples at $W_o = 0.4$ and 0.5. $\Delta E^*$ is higher for the sample at $W_o = 0.4$, indicating a higher detergency for this sample than that of the sample at $W_o = 0.5$. This was observed in spite of the lower oil content present in the sample at $W_o = 0.4$. If we recall the SAXS results, the sample at $W_o = 0.4$ indicated a larger domain size for water and possibly larger oil domain size. In the present detergency test, the model dirt is lipstick, which is mainly composed of solid oil (wax). Results indicate that better detergency was provided by the sample at $W_o = 0.4$, which may be attributed to the larger oil domain size in this sample that allows to dissolve more wax containing dirt during the detergency process. Note that the $\Delta E^*$ values for $W_o = 0.4$ and 0.5 are significantly different, as confirmed by the Student’s $t$-test.

Conclusions

BMEs that have both water and oil continuous phases can be used as a high-performance make-up remover having both reasonable usability and detergency. In this study, we successfully formulated a BME with an ester-type oil and C10. Phase studies and PFG-NMR measurements, along with SAXS measurements, revealed that BMEs are formed in the water/tetra(oxethylene)dodecyl ether ($C_{12}EO_4$/C10 system. Cleansing tests have shown that such BMEs exhibit a better performance for lower oil contents, which was a surprising result as the oil content was considered to be a key factor for detergency. As SAXS results showed that a larger oil domain size in BMEs is required for better cleansing performance, it is hence proved that the structure of the microemulsions is an important issue.
factor that determines the detergency of microemulsions.

References