Preparation of Highly Stable Oil-in-Water Emulsions with High Ethanol Content Using Polyglycerol Monofatty Acid Esters as Emulsifiers

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Abstract: Oil-in-water (O/W) emulsions containing ethanol have been used in food, cosmetics, paints, and other applications. However, O/W emulsions with long-term stability are difficult to produce at high ethanol concentrations because the adsorption of the emulsifier at the O/W interface is restricted by ethanol. In this study, to resolve this issue, we prepared ethanol-containing O/W emulsions with high dispersion stability using a series of polyglycerol monofatty acid esters (PGFEs) with different fatty acid chain lengths, which are bio-safe nonionic surfactants, as emulsifiers. First, aqueous PGFE solutions containing 0–50 wt% ethanol were prepared and then O/W emulsions were formed using limonene as the oil phase. When decaglycerol stearic acid ester (DGMS, C18) was used as the emulsifier, an O/W emulsion with fine droplets (~30 nm in size) was successfully obtained at an ethanol concentration of 35 wt%. This emulsion remained stable for more than four weeks, during which no phase separation occurred, indicating its high dispersion stability. Furthermore, aqueous DGMS solutions containing 30–40 wt% ethanol were viscous, and a lamellar liquid crystal phase was observed to be dispersed in these solutions. The formation of this lamellar liquid crystal phase at the O/W interface led to an interfacial film with superior viscoelastic properties. The results suggested that the stability of the emulsions was determined by the balance between the decrease in interfacial tension caused by the addition of ethanol and the density (rigidity) of the DGMS film formed at the O/W interface. Finally, to further improve the dispersion stability of the ethanol-containing O/W-type emulsions, O/W emulsions were prepared using a mixture of two PGFEs with different degrees of glycerol polymerization, that is, systems having different hydrophilic–lipophilic balance values.

Key words: oil in water emulsion, polyglycerol monofatty acid ester, ethanol containing emulsion, limonene

1 Introduction

An emulsion is a colloidal system consisting of two immiscible liquids, such as water and oil, in which one of the liquids is dispersed as fine particles in the other continuous phase. Emulsions are used in several applications, such as in foods, cosmetics, pharmaceuticals, and paints, because they can add high value that cannot be obtained with a single phase. However, emulsions are thermodynamically unstable systems because their formation results in an increase in the area of the water/oil interface, and hence the interfacial free energy. Ethanol is a solvent with excellent bactericidal properties that is added not only to alcoholic beverages, but also to various foods and household products. Oil-in-water emulsions (O/W emulsions) consisting of ethanol in the aqueous phase have also attracted considerable attention because of their various applications, such as emulsified flavors used in the preparation of alcoholic beverages and water-soluble paints with quick-drying properties. However, when a solvent that has affinity to both water and oil phases, such as ethanol, is added to the emulsion, the emulsion destabilizes because the added solvent decreases the amount and orientation of the surfactant (emulsifier) adsorbed at the W/O interface, weakens the interfacial membrane, and promotes coales-
Previously, ethanol-containing O/W emulsions stabilized using a protein, such as sodium caseinate, as the emulsifier have been prepared\(^7\)-\(^11\). Ethanol-containing emulsions stabilized with Tween 80\(^{12,13}\), a nonionic surfactant often used as a food emulsifier, have also been developed. However, in these cases, the droplet size increased significantly at high ethanol concentrations (higher than 30 or 40 wt%), and it was difficult to obtain an O/W emulsion with high dispersion stability. Conversely, in recent years, ethanol-containing emulsions with relatively high dispersion stability have been developed with a relatively high concentration of ethanol by optimizing the molecular structures of emulsifiers to ensure that their interfacial activities are not easily affected by ethanol. For example, emulsions have been developed using polyoxyethylene-hydrogenated castor oil\(^6\) or gum ghatti/gum arabic\(^8\) as the emulsifier. However, the relationship between the molecular structure of the emulsifier or its hydrophilic–lipophilic balance (HLB) and the dispersion stability of ethanol-containing emulsions has not been investigated in detail.

In this study, we prepared ethanol-containing O/W emulsions using a series of polyglycerol fatty acid esters (PGFEs), nonionic surfactants, as emulsifiers. The PGFEs were obtained by the dehydration–condensation of polyglycerol and fatty acids of different chain lengths. The HLB of the PGFE could be tuned by changing the (i) polymerization degree of polyglycerol, the hydrophilic component, (ii) carbon chain length of the fatty acid, the hydrophobic component, and (iii) degree of esterification. PGFE has high bio-safety because its raw materials are derived from natural sources and are approved as food additives\(^14,15\). PGFEs are used as emulsifiers, solubilizers, and quality improvers for preventing chocolate blooming and reducing viscosity, as well as fat and oil crystallization inhibitors and accelerators\(^15\). Additionally, other favorable features include their excellent heat resistance, and anti-fog and antibacterial properties. Further, PGFEs are applied in cosmetics, pharmaceuticals, and foods, rendering them versatile surfactants\(^16\).

In this study, we prepared ethanol-containing O/W emulsions using PGFEs with different carbon chain lengths as emulsifiers, and investigated the effects of the molecular structure of the emulsifier and ethanol concentration on the dispersion stability. In particular, this study focused on developing an emulsion with excellent dispersion stability and a high ethanol content, ranging up to 40 wt%, which is required for the preparation process of alcoholic beverages.

The dispersion stabilities of O/W and water-in-oil (W/O) emulsions are often improved when they are prepared using a mixture of two or more emulsifiers with different HLB values, as compared with emulsions prepared with a single surfactant\(^17\). Using a mixed surfactant system, the HLB can be tuned closer to the required HLB of the oil phase\(^17\). Thus, the stability of O/W emulsions can be improved even at a high ethanol content using a mixture of PGFEs to increase the adsorption density of the emulsifiers at the O/W interface. Accordingly, emulsions were prepared using mixtures of two PGFEs with different average degrees of glycerol polymerization, that is, different HLB values, and further improvement of the dispersion stability of the ethanol-containing O/W-type emulsions was achieved.

\section*{2 Materials and Methods}

\subsection*{2.1 Materials}

Four PGFEs with a fixed average polymerization degree of 10 and different alkyl chain lengths (n): decaglycerol monolaurate (DGML, n = 12), decaglycerol monomyristate (DGMM, n = 14), decaglycerol monopalmitate (DGMP, n = 16), and decaglycerol monostearate (DGMS, n = 18), were used as emulsifiers. They were kindly provided by Nikko Chemicals Co., Ltd., Japan. Furthermore, an analog of DGMS, diglycerol monostearate (DIGMS) with a glycerol polymerization degree of 2 and alkyl chain length of 18, was used to prepare a mixed emulsifier system. The HLB values of these PGFEs are summarized in Table 1.

As the oil phase, limonene (abbreviated as LN; T. HASEGAWA Co., Ltd.), which is a fragrant oil, was used. Ultrapure water (>18.2 M\(\Omega\) cm, Millipore Direct-Q UV5) was used as the aqueous phase. First-grade ethanol was purchased from Fujifilm Wako Pure Chemical Co. (Japan).

\subsection*{2.2 Preparation of emulsions}

The emulsifier, PGFE was weighed in a 50 mL vial, and desired amounts of ethanol and water were added. The mixture was then heated and stirred to obtain a homogeneous solution. Thereafter, the solution was allowed to cool to room temperature to obtain a PGFE suspension. Subsequently, LN was added to the aqueous suspension to obtain a total weight of the mixture of 25 g. The resulting mixture was then stirred at 3000 rpm for 1 min using a vortex mixer (Vortex MS3 Basic, IKA Co., Ltd.), followed by ultrasonication with a probe-type ultrasonic homogenizer (US-2).

\begin{table}[!h]
\centering
\caption{HLB values of the PGFE used in this study.} 
\begin{tabular}{llll}
\hline
PGFE & Types of fatty acids & Average polymerization degree of glycerol & HLB \\
\hline
DGML & Lauric acid (C = 12) & 10 & 15.5 \\
DGMM & Myristic acid (C = 14) & 10 & 14.0 \\
DGMP & Palmitic acid (C = 16) & 10 & n.a. \\
DGMS & Stearic acid (C = 18) & 10 & 12.0 \\
DIGMS & Stearic acid (C = 18) & 2 & 5.0 \\
\hline
\end{tabular}
\end{table}
Stable Oil-in-Water Emulsions in an Aqueous Ethanol Solution

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300T, 20 kHz, NIHONSEIKI KAISHA Ltd.) for 5 min under ice-cooling conditions. The composition of the emulsion was fixed at emulsifier/LN/ethanol aqueous solution = 1/1/98 wt%. The resulting emulsion was transferred to a 30 mL vial with polytetrafluoroethylene/nitrile packing and stored at 25°C.

2.3 Evaluation methods

2.3.1 Evaluation of the aqueous PGFE dispersion

2.3.1.1 Interfacial tension measurement

The interfacial tension between the aqueous ethanol solutions containing DGMS and LN was measured at 25°C using a pendant-drop type surface tension meter (Solid–Liquid Interface Analysis System DropMaster 500, Kyowa Interface Science Co., Ltd.). A droplet of the PGFE dispersion was added to bulk LN using a syringe, and the interfacial tension was determined from the analysis of the droplet shape using the Young–Laplace method.

2.3.1.2 Small- and wide-angle X-ray scattering (SWAXS) studies

SWAXS measurements were performed to investigate the structure of the molecular aggregates formed in PGFE suspensions. The SWAXS measurements were performed using a system equipped with an Anton Paar SAXSess camera, PANalytical PW3830 laboratory X-ray generator, multilayer film Goebel mirror, block collimator, semi-transparent beam stop, TCS120 temperature controller, and imaging plate detector. The apparatus was operated at 40 kV and 50 mA using Cu-Kα X-rays (wavelength: 0.154 nm). The X-ray irradiation time was 30 min at 25°C.

2.3.2 Evaluation of emulsions

2.3.2.1 Dynamic light scattering (DLS)

The size distribution of the emulsion droplets was determined using a Litesizer 500 instrument (Anton Paar, Graz, Austria). A 1 x 1 cm glass or quartz cuvette containing 1 mL of the emulsion was placed in the sample holder. The measurements were performed at 25°C using 658 nm laser light produced using a single-frequency laser diode.

2.3.2.2 Freeze-fracture transmission electron microscopy (FF-TEM)

The size and morphology of the emulsion droplets were investigated using the FF-TEM technique. The emulsions were quickly frozen in liquid nitrogen (Leica EMCP), and then, the frozen samples were fractured in a freeze-replica apparatus FR-7000A, Hitachi High-Technologies Co.) at −120°C. The sample replica was prepared using carbon shadowing followed by platinum shadowing. After cleaning with acetone and water, the replica was placed on a TEM copper grid coated with holey carbon film. The FF-TEM observations were performed using an H-7650 instrument (Hitachi High-Technologies Co.) at an accelerating voltage of 100 kV under a low electron dose.

3 Results and Discussion

3.1 Preparation of ethanol-containing O/W-type emulsions using PGFEs with different carbon chain lengths as emulsifiers

Ethanol-containing O/W emulsions were prepared using DGML (carbon chain length, 12), DGMM (carbon chain length, 14), DGMP (carbon chain length, 16), or DGMS (carbon chain length, 18). The appearance of each emulsion is shown in Fig. 1. The ethanol concentration (Cmin) corresponding to the lowest turbidity of the emulsion, i.e., the formation of the finest emulsion droplets, was observed to differ for different PGFEs. The Cmin was 20 wt% for DGML, 30 wt% for DGMM, and 40 wt% for DGMP and DGMS. These results suggest that emulsions with the finest droplet size were obtained at higher ethanol concentra-

![Fig. 1](image-url) Appearance of the ethanol-containing O/W emulsions prepared using PGFE with different carbon chain lengths (Top: Immediately after preparation (0W), Bottom: 1 week after preparation (1W)).
tions upon increasing the alkyl chain length of the PGFE.

Conversely, the appearance of the emulsions one week after their preparation showed a characteristic trend that depended on both the alkyl chain length of the PGFE and the ethanol concentration. For each PGFE system, phase separation occurred at an ethanol concentration higher than \( C_{\text{min}} \), and the emulsions were destabilized within one week. In contrast, at \( C_{\text{min}} \), an increase in turbidity was observed after one week; however, phase separation was not observed. In particular, at ethanol concentrations slightly lower than \( C_{\text{min}} \), the turbidity of the emulsions prepared with DGMP (30 wt\%) and DGMS (20 and 30 wt\%) decreased; that is, the emulsions became more transparent than they were immediately after preparation. When DGMS with the longest alkyl chain was used as the emulsifier, a bluish-white solution was obtained at an ethanol content of 30 wt\%, and the dispersibility of the emulsion was maintained for at least four weeks. Thus, DGMS (C18) was selected as the best emulsifier for a more detailed study.

First, to examine the effect of the ethanol concentration on the stability of the DGMS system in more detail, an emulsion was prepared at an ethanol concentration of 35 wt\%. The appearance of the emulsion is shown in Fig. 2, together with those of the 30 and 40 wt\% cases. As shown in Fig. 2, immediately after preparation, the turbidity of the DGMS-based emulsions decreased with increasing ethanol concentration, and the lowest turbidity (highest transparency) was obtained at 35 wt\%, after which the turbidity increased again with a further increase in the ethanol concentration. Similar changes in turbidity with increasing ethanol concentration have also been reported by Saberi et al.\(^{13}\) In contrast, one week after preparation, the emulsions showed the following characteristic behaviors: at ethanol concentrations of 0 and 10 wt\%, turbid emulsions were formed, and there was no change in their turbidity even after four weeks (Fig. 1). At ethanol concentrations of 20 and 30 wt\%, the turbidity gradually decreased with time. Further, at an ethanol concentration of 35 wt\%, the initially observed high transparency of the emulsion was maintained even after one week. However, at an ethanol concentration of 40 wt\%, the turbidity increased with time. Meanwhile, almost no change in turbidity was observed at 50 wt\% ethanol; however, the oil phase, LN, phase-separated approximately one week after the preparation of the emulsion.

The time-dependent changes in the average particle sizes of the DGMS emulsions with different ethanol concentrations were studied using DLS, and the results are shown in Fig. 3. At ethanol concentrations of 0 and 10 wt\%, the particle sizes were approximately 120 and 180
nm, respectively, and almost no change in particle size was observed after 4 weeks and no phase separation was noted.

At ethanol concentrations of 20 and 30 wt%, the particle size gradually decreased from 118 to 87 nm (20 wt%) and 117 to 27 nm (30 wt%), which is consistent with the decrease in turbidity mentioned above. Notably, the particle size distribution gradually turned bimodal, with the peak particle sizes being approximately 10 and 100 nm, and there was a tendency for the smaller particles to increase in size and the latter particles to decrease in size over time (the data for the 30 wt% case are shown in Fig. 4). These peak size values are thought to correspond to solubilized micelles and emulsified droplets of LN, respectively. In the presence of ethanol, the solubilization of LN in the DGMS micelles is promoted, and the size of the solubilized micelles gradually increases. Conversely, the size of the coexisting emulsified droplets gradually decreases because some of the emulsified LN molecules move to the swollen DGMS micelles and are solubilized. A similar phenomenon in which an oil phase transfers from emulsion droplets to swollen micelles as a solubilizate has been reported in the absence of ethanol\(^{18,19}\). In this study, this phenomenon was observed only for systems with 20 to 30 wt% ethanol, and the reason is not clear. However, the phenomenon became more remarkable for our systems because the oil solubilization limit generally increases in the presence of ethanol. Notably, the systems with 20–30 wt% ethanol and 35 wt% ethanol finally phase-separated after one month and two months, respectively, suggesting that they were not thermodynamically stable microemulsions.

At relatively high ethanol concentrations (40%), the particle size was as small as 100 nm or less immediately after the preparation of the emulsions; however, the particle size increased with time. Additionally, the particle size of the system with 50 wt% ethanol was relatively large immediately after preparation, and then increased with time, and the emulsion was destabilized because of coalescence.

In summary, the DLS study confirmed that, at an ethanol concentration of 35 wt%, a stable emulsion with a fine particle size of 20–30 nm was formed immediately after emulsification. The particle sizes determined by DLS were further confirmed by FF-TEM observations (see Fig. 5). The emulsion with 35 wt% ethanol maintained its excellent dispersion stability for more than one month. In the case of a Tween 80 system reported by Saberi et al.\(^{13}\), the ethanol-containing emulsions were found to gradually destabilize over time, whereas excellent dispersion stability was obtained for the present system using DGMS. This result suggests that the improved dispersion stability of our system is due to the characteristics of DGMS used as an emulsifier\(^{13}\).

Next, to study the stabilization mechanism of the ethanol-containing emulsions prepared using DGMS, the properties of LN-free aqueous PGFE solutions were investigated. First, the interfacial tension between the aqueous PGFE (1 wt%) solution and LN was measured (Fig. 6). The Fig. 4 Time-course change in the particle size distributions of PGFE emulsion containing EtOH 30 wt% measured by DLS.

Fig. 5 FF–TEM image of the O/W emulsion at an ethanol concentration of 35 wt% prepared using DGMS.

Fig. 6 Interfacial tension between the aqueous ethanol solutions and LN with and without DGMS at 25°C.
data for ethanol concentrations of 35 wt% or more are not plotted because the interfacial tension was considerably small, and it was impossible to accurately measure it using the experimental setup used. Additionally, to elucidate the effect of the PGFE, the interfacial tension between the aqueous ethanol (without DGMS) and LN are also plotted. As shown in Fig. 6, the interfacial tension was significantly reduced for ethanol concentrations at which fine and stable emulsions could be produced (30–40 wt%).

Figure 7 shows the visual appearance and polarized images of aqueous ethanol solutions containing 1 wt% DGMS at different ethanol concentrations. When ethanol was added to the aqueous DGMS solution, highly viscous mixtures were obtained at 30–40 wt% ethanol content. Additionally, anisotropy was observed for these systems, as shown in the polarized images, suggesting the formation of anisotropic molecular assemblies. To analyze these anisotropic molecular assemblies in more detail, SWAXS measurements were performed for samples with high ethanol concentrations of 30 to 40 wt%. The scattering profiles in Fig. 8 exhibit peaks with a q value of 1:2 in the small-angle region and a peak at 15 nm⁻¹ in the wide-angle region. These results suggest that a lamellar gel was dispersed in the DGMS suspension at ethanol concentrations of 30 to 40 wt%. The lamellar gel formation at relatively high ethanol concentrations is considered to be due to the change in the hydration state of the DGMS. When the temperature of the aqueous DGMS solutions was increased, they became turbid at relatively low temperatures with increasing ethanol concentration. This result indicated that the dehydration of the hydrophilic moiety of DGMS occurred more easily at relatively high ethanol concentrations. This corresponds to a decrease in the number of water molecules that hydrate the hydrophilic groups of the DGMS as the ethanol concentration is increased. Therefore, the critical packing parameter of the DGMS molecule increased as the ethanol concentration increased, resulting in the transformation of the micellar system to a lamellar gel with a planar geometry, that is, to a system with a relatively small curvature.

Based on the foregoing results, the nature of the ethanol-containing O/W emulsion stabilized by DGMS and its stabilization mechanism are discussed. The emulsification process of this system is illustrated in Fig. 9. The particle sizes measured immediately after preparation suggested that an emulsion with the minimum particle size was obtained at 35 wt% ethanol. Therefore, two factors are considered to affect the initial particle size of the emulsion droplets. One is the interfacial tension and the other is the density of DGMS adsorbed at the O/W interface. As shown in Fig. 6, the interfacial tension decreased with increasing ethanol concentration. In contrast, the added ethanol, which has affinity for both the aqueous and oil phases, restricts the adsorption of the surfactant by entering the gaps between the surfactant molecules oriented at the interface. In this system, ethanol is considered to invade the gaps between the oriented DGMS molecules at the O/W interface, and the amount of adsorbed DGMS at the interface decreases as the ethanol concentration increases. Therefore, the particle size observed immediately after emulsification is determined by the balance between these two factors. When the ethanol concentration was low, the contribution of the decreased interfacial tension was large; therefore, the turbidity and size of the emulsion droplets decreased as the ethanol concentration was increased up to 35 wt%. Conversely, when the ethanol content was
higher than 35 wt %, the contribution of the decrease in the adsorbed amount of DGMS was greater than that of the decrease in the interfacial tension; thus, the viscoelasticity of the adsorbed film at the droplet interface decreased, and the emulsion droplets coalesced easily.

For the DGMS system, O/W-type emulsions with small particle sizes and excellent dispersion stabilities were successfully obtained at ethanol contents of 30–35 %. This is advantageous over the previously reported system using Tween 80 \[\text{Twee}n~80\]. In general, to improve the dispersibility of an emulsion, it is necessary to prevent four destabilization processes: creaming, agglomeration, coalescence, and Ostwald ripening. In the ethanol-containing O/W emulsions stabilized by DGMS, coalescence is considered to be the main destabilizing process \[\text{DGMS}\]. Therefore, it is important to investigate if the adsorbed film at the O/W interface can be strengthened, even in the presence of ethanol. It is generally assumed that the amount of adsorbed surfactant decreases as the ethanol concentration increases, and thus, the viscoelasticity of the interfacial film decreases as the ethanol concentration increases. Nevertheless, the O/W emulsion prepared with DGMS remained stable even at a relatively high ethanol concentration of 35 wt %, and oil droplet coalescence did not occur for at least four weeks. This stabilization is considered to be due to the formation of a lamellar gel in the aqueous ethanol solution, peculiar to DGMS or other polyglycerol fatty acid esters with long alkyl chains. In fact, when micron-sized emulsion droplets were prepared by gentle mixing, a maltase cross, characteristic of a lamellar structure, was noted during polarized microscopy observations. Therefore, we infer that the adsorbed surfactant film at the O/W interface was sufficiently strengthened because the lamellar gel dispersion was effectively adsorbed to form a densely oriented adsorbed film. Although the lamellar gel structure was also formed in the aqueous solution containing 40 wt % ethanol, DGMS no longer sufficiently adsorbed to the interface because the solubility of LN in the aqueous phase increased, resulting in a destabilization process due to Ostwald ripening, in addition to coalescence. As a similar increase in viscosity or lamellar gel formation was not observed in the presence of ethanol for oxyethylene-based nonionic surfactants, this stabilization mechanism for O/W emulsions with ethanol is a unique phenomenon observed with PGFE (DGMS) used as the emulsifier.

3.2 Preparation of ethanol-containing O/W-type emulsions using a PGFE mixture as the emulsifier

We attempted to further stabilize the LN-in-water emulsions with a relatively high ethanol content using a mixture of PGFEs to achieve optimal HLB. Emulsions were prepared using DGMS mixed with a more hydrophobic analog, DIGMS, at different ratios; the ethanol concentration was

<table>
<thead>
<tr>
<th>DGMS: DIGMS</th>
<th>100:0</th>
<th>90:10</th>
<th>80:20</th>
<th>50:50</th>
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<tr>
<td>Soon after preparation</td>
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<td>4 months</td>
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Fig. 10 Appearance of the ethanol-containing O/W emulsion prepared using a mixture of DGMS and DIGMS (ethanol content: 40 wt %).
fixed at 40 wt%. The visual appearances of these emulsions are shown in Fig. 10. The emulsions with the mixed emulsifier at DGMS:DIGMS ratios of 100:0, 90:10, and 80:20 (low DIGMS content) appeared bluish immediately after emulsification, while those prepared with a relatively high DIGMS content (up to 50:50) were significantly turbid.

Figure 11 shows the particle sizes of the bluish emulsions obtained using the mixed emulsifier (DGMS:DIGMS ratio = 100:0 to 80:20) immediately after emulsification. The average droplet size of the emulsions decreased with an increase in the proportion of the relatively more hydrophobic DIGMS. Upon storing for one month, the visual appearance, particle size, and dispersibility of the bluish emulsions did not change significantly, irrespective of the composition. However, after four months, only the emulsion stabilized using the emulsifier mixture at a DGMS:DIGMS ratio of 80:20 maintained the dispersion stability without exhibiting creaming-induced destabilization.

The stabilization of the emulsions with a mixed surfactant can be attributed to the properties of the PGFE solutions before emulsification. As previously mentioned, highly viscous solutions were obtained when DGMS was dissolved in 40 wt% ethanol/water, and lamellar liquid crystals were formed in this mixture. This lamellar liquid crystal formation in aqueous ethanol solutions was promoted upon the addition of the more hydrophobic DIGMS, resulting in the formation of a more rigid adsorbed film at the O/W interface. Additionally, the HLB value of the DGMS/DIGMS mixture approached that required for the emulsification of LN in the aqueous solution with 40 wt% ethanol. The required HLB value for emulsifying LN in water has been reported to be 15.0, and the HLB value of the DGMS/DIGMS mixture (80:20 composition) calculated from the weight ratio and HLB value of each surfactant is 10.6. Suzuki et al. reported that the required HLB values of nonionic surfactants for liquid paraffin decreased in the presence of ethanol. Thus, the difference between the required HLB of LN and that of the DGMS/DIGMS mixture can be explained by considering that the required HLB value of LN decreased in the presence of ethanol.

In summary, LN-in-water emulsions could be stabilized even in the presence of a large amount of ethanol (40 wt%) using a mixture of a hydrophilic PGFE (DGMS) and more hydrophobic PGFE (DIGMS), because a rigid interfacial film of the emulsifier mixture was formed at the oil/aqueous ethanol solution interface.

4 Conclusions

We successfully prepared oil (LN)/water emulsions with excellent dispersion stability at high ethanol contents using PGFEs, nonionic surfactants with high biosafety, as emulsifiers. In particular, DGMS (C18) with the longest alkyl chain among the studied PGFEs afforded fine emulsions with high dispersion stability, which were stable even after one month of storage, at a high ethanol concentration of 35 wt%. The high dispersion stability of this system is due to the decrease in the interfacial tension caused by the addition of ethanol and the formation of a dense adsorbed film of the DGMS emulsifier at the O/W interface. Particulate lamellar liquid crystals were observed in 30–40 wt% aqueous ethanol solutions added with DGMS before emulsification, which contributed to the formation of an interfacial film with high density and viscoelasticity at the O/W interface.

LN-in-water emulsions could be further stabilized (for more than four months) even at 40 wt% ethanol content using a mixture of a hydrophilic PGFE (DGMS) and more hydrophobic PGFE (DIGMS) because such mixtures could form a more rigid interfacial film at the oil/aqueous ethanol solution interface. Stable O/W emulsions with a high ethanol content prepared using PGFEs as emulsifiers are expected to be applied in formulations of foods, cosmetics, and paints that use natural resources with less environmental impact than those prepared with emulsifiers derived from petroleum products.

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Conflict of Interest

The authors declare there are no conflicts of interest.
References


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