Bicontinuous Microemulsion Type Cleansing Containing Silicone Oil. II.
Characterization of the Solution and Its Application to Cleansing Agent

Kei WATANABE[1]*, Akira NODA[1], Masahiko MASUDA[1], Tomoko KIMURA[1],
Kazuo KOMATSU[1] and Kazuyoshi NAKAMURA[2]

[1] *Shiseido Co. Ltd., Research Center (Shin-yokohama)*
(Hayabuchi 2-2-1, Tsuzuki-ku, Yokohama 224-8558, JAPAN)
[2] *NiigataUniversity, Faculty of Education & Human Science*
(Igarashi-ninocho 8050, Niigata, JAPAN)

Abstract: In this study, bicontinuous microemulsions (D phase) was prepared by mixing decamethyl cyclopentasiloxane (DC), which is a good solvent for silicone soils, with cosmetic grade alkyl type surfactant polyoxyethylene (8 mol) glyceryl monoisostearate (PGMI) and ethanol aqueous solution. In the pseudo ternary phase diagram of DC/PGMI/15% ethanol aqueous solution system, a ME region exists from the water corner to the center of the ternary diagram. The ME solution solubilizes at most 15% of DC. However, by replacing half the amount of DC by a polar oil cetyl isooctanoate (CIO), the ME region extended continuously from the aqueous corner to the oil-rich region (60% DC). Self-diffusion coefficient measurement by using NMR and FF-TEM observation indicated a bicontinuous structure that solubilizes a large amount of oil and water for the oil-water ratios between 3/7-7/3. Detergency of cosmetic soils containing polymeric siloxane in the ME solution showed the highest value between the oil-water ratios of 1/1 and 7/3, where the ME with bicontinuous structure exists. These results show that bicontinuous type ME containing DC provides a good solution for cleansing silicone soils.

Key words: bicontinuous microemulsion, FF-TEM, phase study, detergency, silicone oil

1 Introduction

Microemulsion consists of a oil/water/surfactant system, which is optically isotropic, (transparent or slightly turbid), low viscous and defined as a thermodynamically stable solubilization system (1-4). It is classified into three types, water-continuous micellar type, bicontinuous type with zero mean curvature structure, and oil-continuous reversed micellar type. Among them, bicontinuous microemulsion (D phase) has been investigated as a fascinating subject (5-11). It is an optically isotropic three-dimensional random multiply connected bilayer

dividing the solvent into two subvolumes. Generally, it is prepared when HLB is balanced. It provides the minimum interfacial tension and the maximum solubilization. Although various structural models have been presented to date, transmission electron microscopy with freeze-fracture replication method (FF-TEM) recently enabled an accurate observation (12-14).

Recently, in addition to the D phase type bicontinuous microemulsion that can contain almost equal amount of oil to water, D' phase in which a surfactant bilayer envelops water to form a network structure was reported (6).

*Correspondence to: Kei WATANABE, Basic Research Center, Shiseido Co., 2-2-1, Hayabuchi, Tsuzuki-ku, Yokohama, 224-8558 JAPAN
E-mail: kei.watanabe@to.shiseido.co.jp

The D phase has been used for tertiary petroleum recovery as an industrial application (15). Basic researches on detergency have been reported by taking advantage of low interfacial tension (16-18). However, no application in the market is known. This article deals with the preparation of D phase containing cyclic siloxane and its detergency of silicone soils.

Earlier papers focused mainly on solubilization of hydrocarbon oil in D phase. Thereafter, studies on phase behavior have been reported on polar oils (19). In the meantime, silicone oil has become particularly important for industrial applications due to its low surface tension, good spread ability on substrates resulting in high protection of skin and hair (20, 21). It would also be of great interest to investigate its detergency of silicone soils.

Studies dealing with phase behavior of systems with silicone oil and silicone surfactants such as polyoxyethylene (POE) trisiloxane/cyclic siloxane/water system (22-26) and graft-type POE-modified silicone surfactant/octamethyl cyclotetrasiloxane/water system (27) were reported in the late 1990s. Silicone surfactants have been used for the reason that the POE alkyl type surfactants are unsuitable for phase study because of extremely low miscibility between dimethyl siloxane and POE chain (solubility parameter: 6.4 and 9.5, respectively). Therefore, very few papers have been published on the combination of POE alkyl type surfactants with silicone oils to our knowledge. In our previous study (28), taking different approach, we used ethanol resulting in improving the miscibility between cyclic siloxane and a POE alkyl type surfactant as well as manipulating HLB. The conditions, structure and properties of the ME phase were discussed by comparing with polar oil.

This article considers the preparation and detergency of D phase containing cyclic siloxane with a POE alkyl type surfactant that is versatile and safe for cosmetic and pharmaceutical use.

2   Materials and Methods

2·1   Materials

POE (8 mol) glyceryl monoisostearate (PGMI) was purchased from Nihon Emulsion (Tokyo, Japan). Cetyl iso-octanoate (CIO) was purchased from Nikko Chemicals (Tokyo). Decamethyl cyclopentasiloxane (DC) was purchased from Shin-Etsu Chemical (Tokyo). For measurements of relative detergency, W/O liquid type foundation containing 3% silicon resin, and a sheet of white artificial leather, with polyurethane surface (Kyowa Seikan, Tokyo), was used.

2·2   Methods

Phase Diagram Determination. Various amount of constituents were poured into test tubes and mixed by a vortex mixer. The samples were stored in water bath at 25℃ and the phase equilibria were determined by visual observation. The optical isotropic nature of the sample was checked with cross polarizers. The type of liquid crystalline phase was determined by using a polarity microscope. The following abbreviations are used: L_1 represents aqueous micellar solution; L_2, reversed micellar solution; L_α, lamellar liquid crystalline phase; I, one-phase region; II, two-phase region. An abbreviation LC is used for multi phase region with an unidentified liquid crystalline phase.

FF-TEM Observation. The freeze-fracture transmission electron microscopy (FF-TEM) observation on the replication of samples was performed by H800 electron microscope (Hitachi, Tokyo). For the preparation of replicas, a small amount of sample was placed on a gold disc. Then, the sample was plunged into liquid nitrogen. The frozen sample was fractured and replicated in a freeze-fracture apparatus BAF 400 (Balzers, Liechtenstein) at -140℃. Pt/C was deposited on the sample at an angle of 30°.

NMR Measurement. The self-diffusion coefficients (D_{sel}) of the sample in this system were measured with a Fourier transform pulsed gradient spin echo technique monitoring the proton NMR spectra (29-31). The samples were sealed in 5 mm tubes, and a NMR spectrometer operating at 300 MHz with a 90-δ-180-δ pulse sequence was used. The self-diffusion coefficient, D_{sel}, of a proton is determined from the decay of its echo amplitude, A, given by the following equation;

$$A = A_0 \exp[-D_{sel} (G\gamma\delta)^2(\Delta-\delta/3)] \tag{1}$$

where A_0 is the echo amplitude in the absence of a magnetic field, γ the proton gyromagnetic ratio, and Δ the interval between field gradient pulses of magnitude G and variable duration δ. The time over which diffusion was followed, defined by Δ, could be varied from 1 to 1000 ms, corresponding to diffusion over distances of 0.1-10 μs for typical values of D_{sel}. During the measurement, Δ and G were kept constant. A linear least-

squares analysis was used, according to equation (1), to extract the diffusion coefficient of specific species when the peak from the protons of that specific species did not overlap with that from any other protons of other species. On the other hand, if two peaks overlapped, a biexponential nonlinear least-square analysis was used.

Viscosity Measurement. They were carried out on the ME phase by using Dynamic Capillary Rheometer DCR (Anton Paar, Graz, Austria).

Small-angle X-ray Scattering (SAXS). Interlayer spacing measurements on a lamellar liquid crystalline phase were performed by a JEOL JDX-3500 (Tokyo).

In Vitro Evaluation of Detergency. The W/O type liquid foundation was applied to a sheet of white artificial leather (approx. 30 × 120 cm) and stored at room temperature for 6 hrs. A square leather (1 × 1 cm) was cut out and dipped into a 100 ml test tube filled with 50 ml of ME with various compositions. The test tube was shaken for 10 min by a paint shaker. After the leather specimen was taken out and dried at room temperature, L value (the brightness index of Commission Internationale del'Eclariage 1976 colorimetric system) of the surface was measured by a color analyzer SE 2000 (Nippon Denshoku, Tokyo, Japan). The relative detergency was calculated by the following equation;

$$S = (L - L_{FD})/(L_0 - L_{FD}) \qquad (2)$$

where L is measured value after cleansing, L_0 is for bare artificial leather, and L_{FD} is measured value after the foundation was applied and dried. If the foundation is removed perfectly, S will become 1, and if all the foundation remains, S will become 0.

3　Results and Discussion

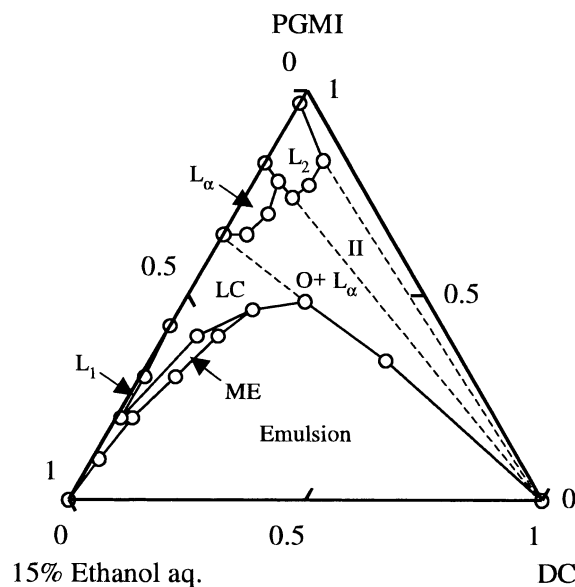### 3·1　Pseudo Ternary Phase Diagram of PGMI/15% Ethanol Aqueous Solution/DC System

To investigate the condition of preparation of bicontinuous type microemulsion phase, a pseudo ternary phase diagram was constructed. In our previous study (28), the miscibility between PGMI and DC was mainly discussed by the pseudo ternary phase diagram. Because of that, PGMI/ethanol mixture was placed at the surfactant corner as a pseudo component. In this study, 15% ethanol aqueous solution is considered as a pseudo component, and placed at the aqueous corner in order to investigate the condition of the preparation in

respect to oil-water ratio and surfactant concentration in addition to the miscibility.

The pseudo ternary phase diagram of PGMI/15% ethanol aqueous solution/DC system is shown in **Fig. 1**. From the ethanol aqueous solution corner, a L_1 region that is unable to solubilize DC extends toward the center of the surfactant-aqueous solution axis. With increasing concentration of PGMI, a LC region exists followed by a L_α 1-phase region. The L_α phase can solubilize at most 8% of DC. At higher concentration of PGMI, a surfactant solution (L_2) region exists. It solubilizes as much as 10% of DC.

Addition of excess amount of oil beyond the limit cause a separation of an oil phase. The reason for the small solubilization limit of DC in the aggregates can be attributed to the small miscibility between PGMI and DC. A considerably large emulsion region (miscibility gap) also indicates the low miscibility.

From the aqueous corner toward the center of the phase diagram, there is a ME 1-phase region where
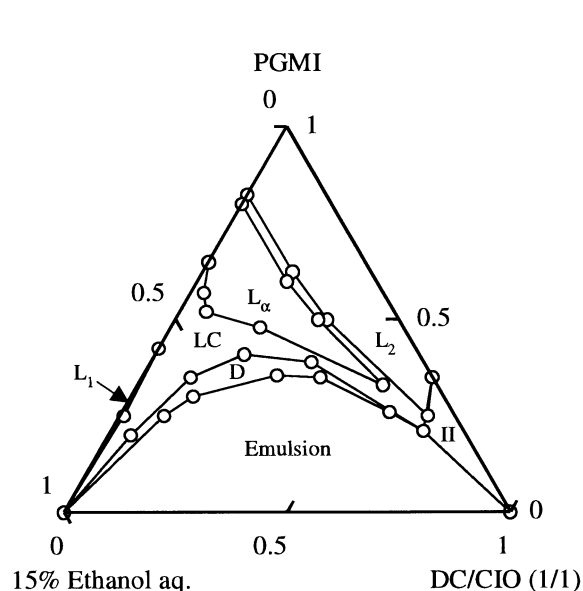

Fig. 1　Pseudo Ternary Phase Diagram of DC/PGMI/15% Ethanol Aqueous Solution System at 25℃. The following abbreviation is used: L_1 represents aqueous micellar solution; L_2, reversed micellar solution; D, bicontinuous microemulsion; L_α, lamellar liquid crystalline phase; I, one-phase region; II, two-phase region. An abbreviation LC is used for a multi phase region with an unidentified liquid crystalline phase.

549

PGMI aqueous solution solubilizes DC. The maximum amount of solubilized DC is 15% in the solution containing 34% water, 45% PGMI and 6% ethanol. The oil-water ratio is approximately 3/7.

3·2 Pseudo Ternary Phase Diagram of PGMI/15% Ethanol Aqueous Solution/DC/CIO System

The pseudo ternary phase diagram of PGMI/15% ethanol aqueous solution/DC/CIO system is shown in **Fig. 2**. It seems to be worthwhile to compare this diagram with that of the system without CIO (**Fig. 1**). The ME region continuously extends toward the oil-rich region. At most 60% of the oil mixture (DC plus CIO) can be solubilized in a ME containing 27% of PGMI, 2% of ethanol and 11% of water. The oil-water ratio is 85/15.

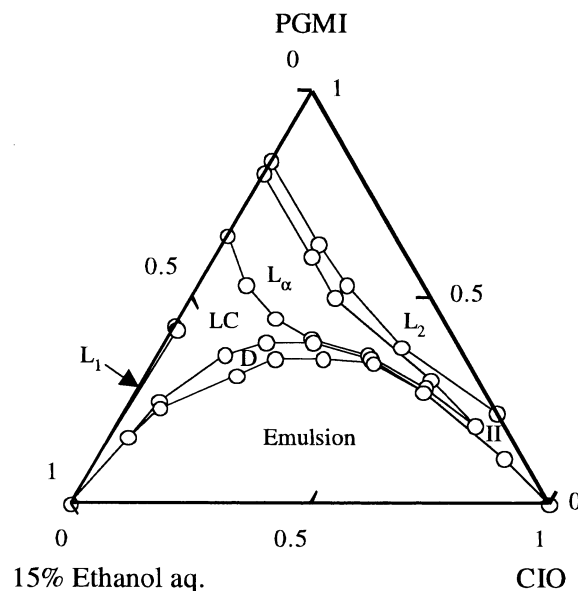The L_α and the L_2 regions also extend toward the oil corner. The emulsion region (miscibility gap) is smaller than that of the DC system. A point to which attention should be addressed is that the addition of CIO provides an improvement of miscibility with PGMI. Consequently, the amount of solubilization in the self-organized structures such as L_α, and ME increased drastically.

Neighboring phases generally show a close structural correlation with ME phase. Between the oil-water ratios of 3/7 and 85/15, the L_α phase is in the close neighborhood across a short intermediate 2-phase region. This leads us to assume a formation of a bicontinuous type ME around the ratio.

3·3 Pseudo Ternary Phase Diagram of PGMI/15% Ethanol Aqueous Solution/CIO System

Phase diagram containing CIO as an oily component (without DC) is shown in **Fig. 3**. The features are similar to that of **Fig. 2**. This also agrees with the result of

Fig. 2 Pseudo Ternary Phase Diagram for DC/CIO/PGMI/ 15% Ethanol Aqueous Solution System at 25℃. The ratio of DC/CIO is 1/1. ME phase extends from the water corner to the oil rich region via center of the phase diagram. The following abbreviation is used: L_1 represents aqueous micellar solution; L_2, reversed micellar solution; D, bicontinuous microemulsion; L_α, lamellar liquid crystalline phase; I, one-phase region; II, two-phase region. An abbreviation LC is used for multi phase region with an unidentified liquid crystalline phase.
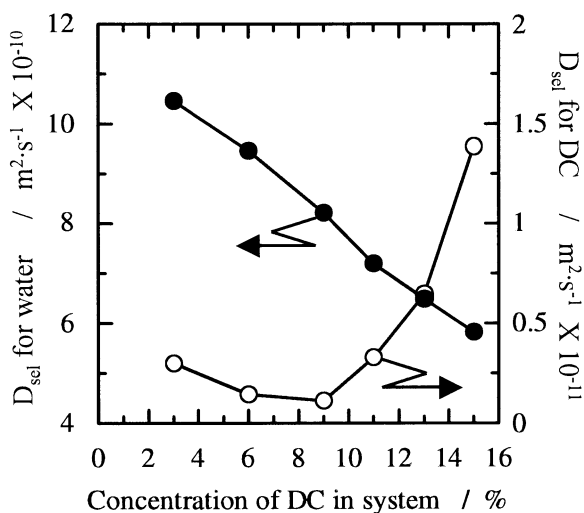

Fig. 3 Pseudo Ternary Phase Diagram for CIO/PGMI/ 15% Ethanol Aqueous Solution System at 25℃. ME phase extends from water corner to oil rich region via the center of the phase diagram. The abbreviation L_1 represents aqueous micellar solution; L_2, reversed micellar solution; D, bicontinuous microemulsion; L_α, lamellar liquid crystalline phase; I, one-phase region; II, two-phase region. An abbreviation LC is used for multi phase region with an unidentified liquid crystalline phase.

550

our previously reported ternary phase diagram system in which ethanol/PGMI mixture is placed at surfactant corner (28). As we have concluded, adding a polar oil such as CIO is an effective method to put self-organized structure containing DC into practical use. In the considered system, the replacing half the amount of DC make it possible to treat the oil in the same manner as CIO system.

3·4 Characterization of the ME Regions by D_{sel} Measurement

It is known that D_{sel} is large when molecules are dispersed in the bulk. When molecular migration is restricted by some structure, D_{sel} becomes small. **Figure 4** shows the D_{sel} for the ME region in the pseudo ternary phase diagram of DC system. D_{sel} for water and DC in the bulk are 3.08×10^{-9} m$^2 \cdot$s and 5.02×10^{-10} m$^2 \cdot$s, respectively. Based on those values, it is obvious that water and DC molecules are restricted in the ME region.

D_{sel} changes continuously depending on the oil-water ratio. D_{sel} for water is relatively high in the water-rich region and decreases monotonically with increasing oil-water ratio. D_{sel} for DC is low in the water-rich region and increases steeply beyond 9% of DC. The increase in the concentration of DC causes a structural change in the surfactant aggregate. The decrease in D_{sel} of water molecules indicates narrowing of the diffusion path for the water molecule, while the increase in the D_{sel} of DC molecules indicates widening the path for the DC molecule. This reveals that the water molecules change their location from the bulk to the bicontinuous microemulsion channels, while the DC molecules move from inside the micelle to the bicontinuous microemulsion channels.

The measurement was also carried out on the DC/CIO system, and the result is shown in **Fig. 5**. D_{sel} for water decreases monotonically depending on the oil/water ratio. The D_{sel} for DC remains low and constant up to a oil-water ratio of 3/7 and then raises steeply. As the DC system (**Fig. 4**), it is quite reasonable to conclude that water and the DC molecules change their location starting from a oil-water ratio of 3/7. Based on the findings from the phase diagram and the D_{sel} measurements, it is assumed that the transformation from a L_1 to the D phase takes place around the ratio of 3/7.

3·5 Characterization of the ME Regions by Viscosity Measurement

The zero shear viscosity of the ME phase was measured to obtain basic data on the solution behavior. It is clear from the **Fig. 6** (DC system) that the viscosity
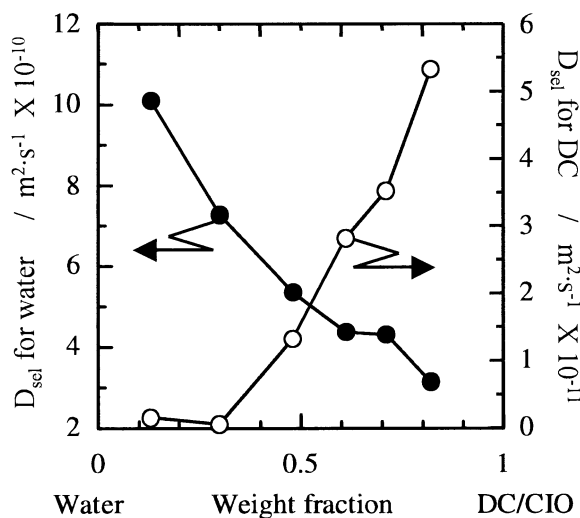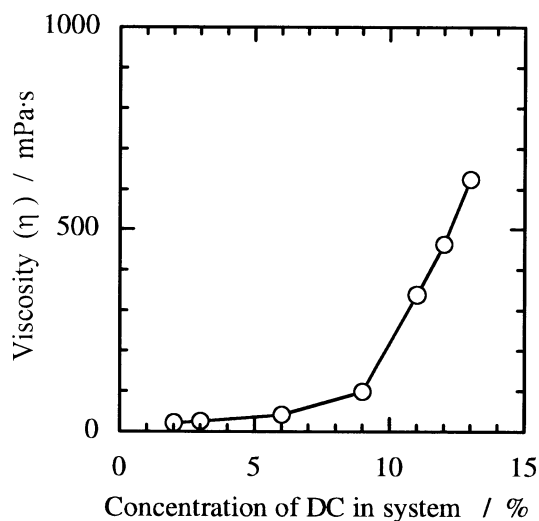
Fig. 4 Correlation between Concentration of DC and D_{sel} for DC (open circles) and Water (closed circles), in ME Prepared from a DC/PGMI/15 % Ethanol Aqueous Solution System.
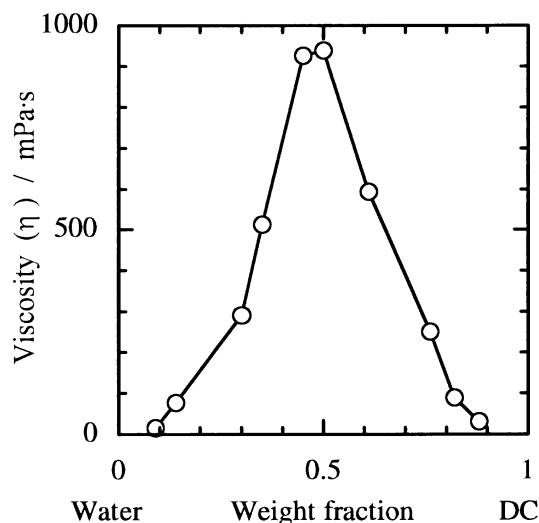
Fig. 5 Correlation between Oil-Water Ratio and D_{sel} for DC (open circles) and Water (closed circles), in ME Prepared in DC/CIO/PGMI/15 % Ethanol Aqueous Solution System.

551

Fig. 6 Zero Shear Viscosity of ME in DC/PGMI/15% Ethanol Aqueous Solution System.

increases steeply from the DC concentration of 9%. The point at which the viscosity start increasing coincide with that of the D_{sel} increase in the same system. It is reasonable to conclude that the results are caused by a steep increase in the aggregation number.

On the other hand, with increasing oil/water ratio in DC/CIO system, the zero-shear viscosity of the ME increases up to a maximum at around 1/1, and then decreases (**Fig. 7**). The maximum value is nearly 1,000 mPa·s, which is 70 times larger than the value of a water-rich solution (14 mPa·s). The maximum viscosity is the reflection of the maximum of the aggregation number at around the ratio of 1/1. Similarly to a water/hydrocarbon oil/nonionic surfactant system, structural changes of aqueous micellar solution (L_1) - bicontinuous microemulsion (D) - reversed micellar solution take place depending on the oil-water ratio.

3·6 Characterization through the Neighboring L_α Phase in the DC/CIO System

The L_α phase in the pseudo ternary system (**Fig. 3**) at a constant surfactant/water ratio of 7/3 was studied by means of small-angle X-ray scattering, and D_{sel} measurement to gain insight on the relationship with the neighboring ME phase.

The correlation between interlayer spacing and the amount of oil is shown in **Fig. 8**. The interlayer spacing d is 7.5 nm in the absence of oil, and increases monotonically with increasing amount of oil, and reaches a maximum of 17 nm at around the phase boundary with the 2-phase region. In this composition range, D_{sel} for water stays constant at 4×10^{-10} m²·s⁻¹, while D_{sel} for oil increases monotonically with increasing concentration of oil (**Fig. 9**). It is reasonable to attribute this result to the uptake of oil between the layers of the lipophilic groups resulting in the broadening of the interlayer spacing.

Fig. 7 Zero Shear Viscosity of ME in DC/CIO/PGMI/15% Ethanol Aqueous Solution System.
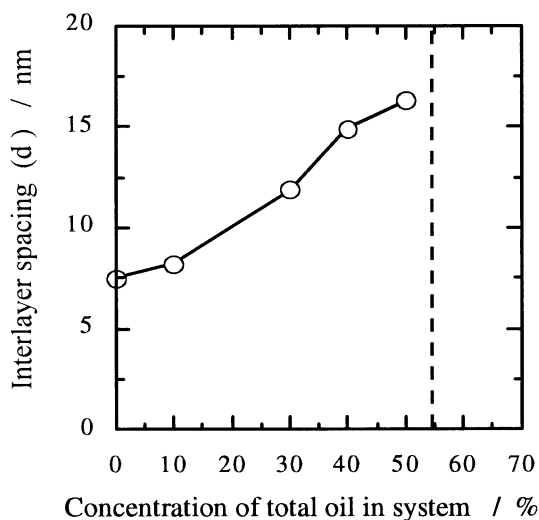
Fig. 8 The Effect of Oil Concentration on the Interlayer Spacing of the L_α Phase at a Constant PGMI/15% Aqueous Solution Ratio of 7/3 in the DC/CIO/ PGMI/15% Ethanol Aqueous Solution System.
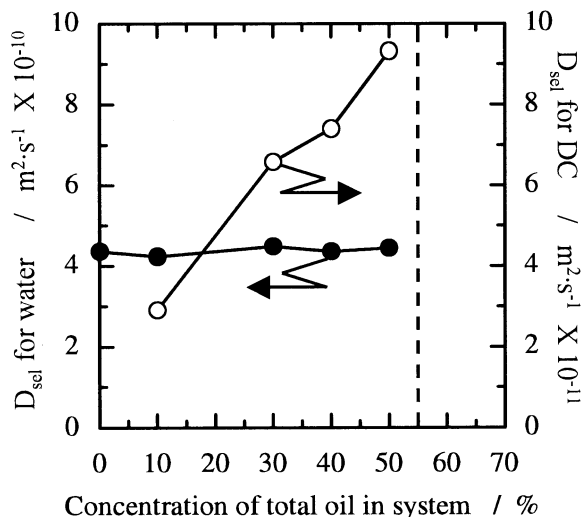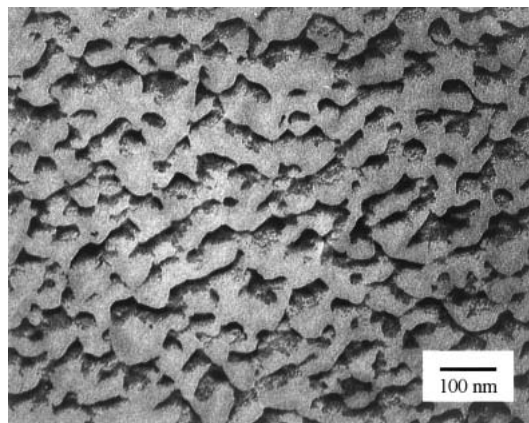
Fig. 9 The Effect of the Oil Concentration on D_{sel} for DC (open circles) and Water (closed circles), in L_α Phase at a Constant PGMI/15% Aqueous Solution Ratio of 7/3 in DC/CIO/PGMI/15% Ethanol Aqueous Solution System.

Fig. 10 Electron Micrograph of a Replica of a ME Solution with Oil-Water Ratio 1:1 in DC/CIO/ PGMI/15% Ethanol Aqueous Solution System. The bar is equal to 100 nm.

It is worthwhile to compare a series of D_{sel} values measured along the ME region and along the L_α 1-phase region, especially above the oil-water ratio of 6/4, where L_α and ME compositions become close to each other. Values of D_{sel} for water in both phases agree well at 4×10^{-10} m$^2 \cdot$s^{-1}. On the other hand, D_{sel} for DC shows similar values that are smaller than free D_{sel} of DC by one order of magnitude. These results suggest a structural correlation between the phases.

3·7 FF-TEM Observation

Electron micrograph from the ME solution with oil-water ratio 1/1 in DC/CIO/PGMI/15% ethanol aqueous solution system is shown in **Fig. 10**. One can observe a typical texture of bicontinuous ME, so-called sponge structure (12). The image of the microstructure of the ME reveals a zero mean curvature structure of the surfactant monolayers between the water and oil channels. In several parts of the micrograph, it is possible to follow the channel over large distances over a micrometer.

By closer observation, oil domains with smooth appearance and aqueous domains with grainy appearance can be discriminated. The smooth areas are fracture faces of the oil domain, whereas the grainy areas were caused by formation of many small ice grains on the aqueous domains that were eroded by etching.

3·8 Detergency of Cosmetic Soils Containing Silicone Resin in the Bicontinuous ME Phase

As discussed above, structural change takes place according to the oil-water ratio. The oil-water ratio dependence on detergency is shown **Fig. 11**. The cosmetic soil contains 3% of silicone resin. While the detergency is relatively low in the water-rich region, it
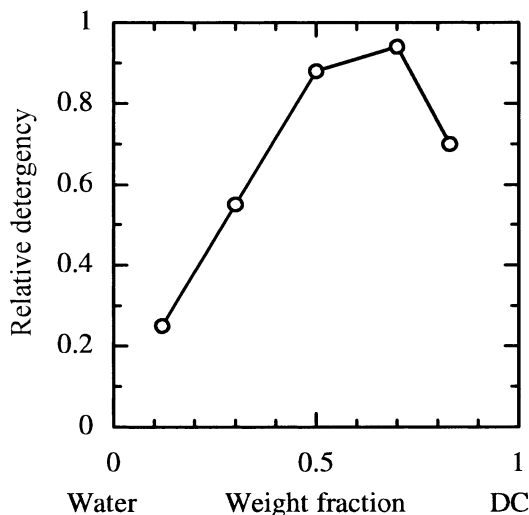
Fig. 11 Correlation between Oil-Water Ratio and Relative Detergency of Cosmetic Soils Containing Silicone Resin in ME Prepared from DC/CIO/PGMI/15% Ethanol Aqueous Solution System.

553

increases according to the oil-water ratio, and passed over maximum at the ratio of 7/3.

Not only the permeability and dispersing ability of ME phase, but also the miscibility of silicone resin with DC should be considered. The ratio of 1/1 to 7/3 seems to be optimum for both factors resulting in excellent detergency.

4 Conclusion

In pseudo ternary phase diagram consisting of a POE alkyl type surfactant PGMI, a cyclic siloxane oil DC, and 15% ethanol aqueous solution system, the self-organized structures such as a ME, a L_α, and a L_2 solubilize small amount of DC. However, by replacing half the amount of DC by a polar oil CIO, these regions extend toward oil corner drastically. This change is due to improvement of the miscibility between PGMI and oil. Self-diffusion coefficient and zero-shear viscosity measurements revealed the transformation from L_1 to bicontinuous type ME. The bicontinuous ME phase with zero mean curvature structure can be prepared beyond the oil-water ratio 3/7. On the other hand, the ME in the pseudo ternary phase diagram shows maximum detergency for oil-water ratios between 1/1 to 7/3. From these results, it is concluded that bicontinuous type microemulsion containing DC is suitable for cleansing cosmetic soil containing silicone resin.

Acknowledgement

References

1. K. SHINODA and S. FRIBERG, *Emulsions and Solubilization*, Wiley-Interscience, New York (1986).

2. J.N. ISRAELACHVILI, *Intermolecular and Surface Forces, with Applications to Colloidal and Biological Systems*, Academic Press, London, p. 247 (1985).

3. H. KUNIEDA and K. SHINODA, Phase Behavior in Systems of Nonionic Surfactant/Water/Oil around the Hydophile-Lipophile-Balance-Temperature, *J. Dispersion Sci. & Tech.*, Vol. **3**, 233-244 (1982).

4. H. KUNIEDA, K. NAKAMURA, H.T. DAVIS and D.F. EVANCE, Formation of Vesicles and Microemulsions in a Water/Tetraethylene Glycol Dodecyl Ether/Dodecane System, *Langmuir*, Vol. **7**, 1915-1919 (1991).

5. K. SHINODA, Solution Behavior of Surfactants: the Importance of Surfactant Phase and the Continuous Change in HLB of Surfactant, *Prog. Colloid Polym. Sci.*, Vol. **68**, 1-7 (1983).

6. H. KUNIEDA, H. ASAOKA and K. SHINODA, Two Types of Surfactant Phases and Four Coexisting Liquid Phases in a Water/Nonionic Surfactant/Triglyceride/Hydrocarbon System, *J. Phys. Chem.*, Vol. **92**, 185-189 (1988).

7. C.A. MILLER, M. GRADZIELSKI, H. HOFFMANN, U. KRAMER and C. THUNIG, Experimental Results for the L_3 Phase in a Zwitterionic Surfactant System and Their Implications Regarding Structures, *Colloid Polym. Sci.*, Vol. **268**, 1066-1072 (1990).

8. R. STREY, W. JAHN, G. PORTE and P. BASSEREAU, Freeze Fracture Electron Microscopy of Dilute Lamellar and Anomalous Isotropic (L3) Phases, *Langmuir*, Vol. **6**, 1635 -1639 (1990).

9. K. WATANABE, Y. NAKAMA, T. YANAKI and H. HOFFMANN, Novel Vesicle and Sponge Phase Prepared in Amphoteric Surfactant/Anionic Surfactant/Oleic Acid/Water System, *Langmuir*, Vol. **17**, 7219-7224 (2001).

10. K. SHINODA and H. SAITO, The Effect of Temperature on the Phase Equilibria and the Types of Dispersions of the Ternary System Compsed of Water, Cyclohexane, and Nonionic Surfactant, *J. Colloid Interface Sci.*, Vol. **26**, 70-74 (1968).

11. H. KUNIEDA and K. SHINODA, Correlation between Critical Solution Phenomena and Ultralow Interfacial Tensions in a Surfactant/Water/Oil System, *Bull. Chem. Soc. Jpn.*, Vol. **55**, 1777-1781 (1982).

12. H. HOFFMANN, C. THUNIG, U. MUNKERT, H.W. MEYER and W. RICHER, From Vesicles to the L3 (sponge) Phase in Alkyldimethylamine Oxide/Heptanol Systems, *Langmuir*, Vol. **8**, 2629-2638 (1992).

13. W. JAHN and R. STREY, Microstructure of Microemulsions by Freeze Fracture Electron Microscopy, *J. Phys. Chem.*, Vol. **92**, 2294-2301 (1988).

14. T. IMAE, T. IWAMOTO, G. PLATZ and C. THUNIG, Electron Microscopic and Light Scattering Observation on a System with Two Iridescent Phases, *Colloid Polym. Sci.*, Vol. **272**, 604-611 (1994).

15. D.O. SHAH and R.S. SCHECHTER, *Improved Oil Recovery by Surfactant and Polymer Flooding*, Academic Press, New York (1977).

16. M. KAHLWEIT and R. STREY, The Phase Behavior of H_2O-Oil-Nonionic Amphiphile Ternary Systems, in *Microemulsion Systems* (H.L. ROSANO and M. CLAUSSE, eds.), Marcel Dekker, New York, pp. 1-13 (1987).

17. M. FUJITSU and T. TAMURA, Fatty Soil Removal in Ionic Microemulsion Systems, *Yukagaku*, Vol. **43**, 131-136 (1994).

18. K.H. RANEY, W.J. BENTON and C.A. MILLER, Optimum Detergency Conditions with Nonionic Surfactants. I. Ternary Water-Surfactant-Hydrocarbon Systems, *J. Colloid Interface Sci.*, Vol. **117**, 286-292 (1986).

19. H. KUNIEDA, Phase behavior in Water/Nonionic Surfactant/

Amphiphillic Oil Systems, *J. Colloid Interface Sci.*, Vol. **133**, 237-243 (1986).

20. J.M. BLAKELY, *The Benefits of Silicones in Facial and Body Cleansing Products*, Dow Corning Publication, Brussels (1994).

21. M.L. SCHLOSSMAN, Decorrative Products, in *Handbook of Cosmetic Science and Technology* (A.O. BAREL, M. PAYE, H.I. MAIBACH, eds.), Marcel Dekker, New York, pp. 645-683 (2001).

22. H. KUNIEDA, H. TAOKA, T. IWANAGA and A. HARASHIMA, Phase Behavior of Polyoxyethylene Trisiloxane Surfactant in Water and Water-Oil, *Langmuir*, Vol. **14**, 5113-5120 (1998)

23. X. LI, R.M. WASHENBERGER, L.E. SCRIVEN, H.T. DAVIS and R.M. HILL, Phase Behavior and Microstructure of Water/Trisiloxane E12 Polyoxyethylene Surfactant/Silicone Oil Systems, *Langmuir*, Vol. **15**, 2267-2277 (1999).

24. M.H. UDDIN, C. RODRIGUEZ, K. WATANABE, A. LOPEZ-QUINTELA, T. KATO, H. FURUKAWA, A. HARASHIMA and H. KUNIEDA, Phase Behavior and Formation of Reverse Cubic Phase Based Emulsion in Water/Poly (oxyethylene) Poly (dimethylsiloxane) Surfactants/Silicone Oil Systems, *Langmuir*, Vol. **17**, 5169-5175 (2001).

25. H. KUNIEDA, M.H. UDDIN, Y. YASHITA, H. FURUKAWA and A. HARASHIMA, Microemulsions in Poly (oxyethylene) Poly (dimethylsiloxane) Copolymer, *J. Oleo Sci.*, Vol. **51**, 113-122 (2002).

26. R.M. HILL, in *Silicone Surfactants* (R.M. HILL, ed.), Surfactant Science Series, Vol. **86**, Marcel Dekker, New York, p. 40 (1999).

27. T. IWANAGA, Y. SHIOGAI and H. KUNIEDA, Phase Behavior of Polyloxyethylene Modified Silicone with Water, *Prog. Colloid Polym. Sci.*, Vol. **110**, 225-229 (1998).

28. K. WATANABE, A. NODA, M. MASUDA and K. NAKAMURA, Bicontinuous Microemulsion Type Cleansing Containing Silicone Oil. I. Comparison of Solubilization Behavior of Cyclic Siloxane with Polar Oil, *J. Oleo Sci.*, Vol. **53**, 537-546 (2004).

29. B. LINDMAN, P. STILBS and M.E. MOSLEY, Fourier Transform NMR Self-Diffusion and Microemulsion Structure, *J. Colloid Interface Sci.*, Vol. **83**, 569-582 (1981).

30. T. KATO, N. TAGUCHI, T. TERAO and T. SEIMIYA, Structure of Networks Formed in Concentrated Solutions of Nonionic Surfactant Studied by the Pulsed-Gradient Spin-Echo Method, *Langmuir*, Vol. **11**, 4661-4664 (1995).

31. F. NILSSON, O. SODERMAN and J. REIMER, Phase Separation and Aggregate-Aggregate Interactions in the C9G1/C10G1 - Alkyl Glucosides/Water System. A Phase Diagram and NMR Self-Diffusion Study, *Langmuir*, Vol. **14**, 6396-6402 (1998).