

# Solution Properties of Homogeneous Polyglycerol Dodecyl Ether Nonionic Surfactants

Hikomichi Sagitani\*, Yoshie Hayashi and Michio Ochiai

Pola Corp., Yokohama Research Laboratories, 27-1, Takashimadai, Kanagawa-ku, Yokohama, Japan

The synthesis and solution properties of a homologous series of polyglycerol dodecyl ethers ( $R_{12}G_n$ ) are described. The phase behavior, surface tension, cloud point and HLB value (hydrophile lipophile balance) of these surfactants in aqueous solutions and in mixed solutions of water/oil have been investigated and compared with values for polyoxyethylene dodecyl ether ( $R_{12}EO_n$ ). The surface tension measurements showed that  $R_{12}G_n$  have sufficiently low values of surface tension and critical micellization concentration (cmc) to serve as useful nonionic surfactants. The mesophases appearing in the  $R_{12}G_n$  systems were more stable in a high temperature range than the mesophases of the  $R_{12}EO_n$  systems. The cloud point and HLB data indicated that addition of one glycerol group was equivalent to the addition of three oxyethylene units, as far as the hydrophilic property was concerned. The phase diagrams of the  $R_{12}G_n$ /dodecane/water systems showed that the solubilizing and emulsifying powers of  $R_{12}G_n$  were greater than those of  $R_{12}EO_n$ . It is concluded that the polyglycerol chain can be even more useful as the hydrophilic part of nonionic surfactants than the conventional oxyethylene chain.

Polyglycerol fatty esters have been available commercially for use in the food industry for almost 30 years. Babayan investigated the application of polyglycerol esters in cosmetics and showed that these surfactants gave stable W/O emulsions (1). Hemker reported that polyglycerol fatty esters formed liquid crystals at the emulsion interface which effectively stabilized the emulsions (2). The HLB can be varied by varying the chain length of the glycerol unit and the degree of esterification of the polyglycerol. McIntyre calculated that the HLB values of polyglycerol fatty esters range from 4 to 15 (3). Polyglycerol fatty esters are useful as cosmetic and food emulsifiers because of the availability of surfactants with a wide HLB range. However, very few studies have been conducted on their physicochemical properties, and the characteristics of the polyglycerol group have not yet been elucidated. The primary reason for this is that polyglycerol esters have so many isomers. Garti studied the composition of so-called "polyglycerol monostearate" (prepared from 1 mol of polyglycerol and 1 mol of stearic acid) and showed the percentage of monoester was 40.7% for triglycerol monostearate, 29.6% for hexaglycerol monostearate and 20.9% for decaglycerol monostearate (4). The Griffin HLB value of decaglycerol monostearate is 14.5 (3). However, the working value of the commercial product is much lower.

To investigate the hydrophilic contribution of glycerol groups in nonionic surfactants, homogeneous polyglycerol monododecyl ethers were synthesized and their solution properties studied. The solubilizing and emulsifying powers

of polyglycerol dodecyl ether were compared against those of polyoxyethylene dodecyl ether by using phase diagrams of the surfactant/water/oil systems.

## EXPERIMENTAL

**Materials.** Glycerol dodecyl ether (Shiono Perfume) was recrystallized twice from petroleum ether and the purity determined by gas chromatography to be greater than 99%. Glycidyl dodecyl ether was donated by Nikko Chemicals, and the purity was also determined by gas chromatography to be above 97%. Glycerol and sodium were obtained from Wako Pure Chemicals. Diglycerol, epichlorohydrin and boron trifluoride ethyl ether were purchased from Tokyo Kasei. Homogeneous hexaoxyethylene dodecyl ether ( $R_{12}EO_6$ ) (Nikko Chemicals) and commercial polyoxyethylene dodecyl ether ( $R_{12}EO_n$ ) (Kao Co.) were used as polyoxyethylene-type nonionic surfactants. Dodecane (Tokyo Kasei) and liquid paraffin (Esso Oil, Crystol 70) were used as oil phases. Sorbitan monostearate and polyoxyethylene (20) sorbitan monostearate were purchased from Toho Chemicals. These materials were used without further purification. Water was deionized and distilled. For the surface tension measurements only, the deionized water was distilled twice immediately before the measurements.

**Synthesis of diglycerol dodecyl ether (II).** Sodium (0.0413 mol, 1 g) was added to anhydrous glycerol (4.13 mol, 380 g) under nitrogen atmosphere, and the solution was heated to 130 C for an hr. Glycidyl dodecyl ether (I) (0.826 mol, 200 g) was added to the sodium glycerate drop by drop over one hr at 180 C. This mixture was stirred magnetically for eight hr. The product was purified on a silica gel (1 kg) column using chloroform/methanol (98/2) as a solvent. The product was recrystallized from petroleum ether to give 95.2 g (35% overall yield) of diglycerol dodecyl ether (II).

**Synthesis of triglycerol dodecyl ether (III).** Sodium (0.061 mol, 1.4 g) was added to anhydrous diglycerol (3.1 mol, 514.6 g) under nitrogen atmosphere, and the solution was stirred at 120 C for one hr. Glycidyl dodecyl ether (I) (0.620 mol, 150 g) was added drop by drop to the sodium diglycerate over 1.5 hr at 180 C. The solution was stirred for three hr, and the paste-like material was purified on a silica gel (1 kg) column using chloroform/methanol (97/3) as solvent. The overall yield was 38% (86.1 g) of triglycerol dodecyl ether (III).

**Synthesis of tetraglycerol dodecyl ether (VI).** Glycerol dodecyl ether (IV) (2.3 mol, 600 g) was dissolved in a solution of boron trifluoride ethyl ether (1 ml) and dichloromethane (1.5 l) at 40 C. Epichlorohydrin (1.2 mol, 111 g) was added to the solution drop by drop, and the solution was stirred for five hr. The solvent was distilled away and the unreacted glycerol dodecyl ether was removed by filtration from petroleum ether. The filtrate was dissolved in a mixed solution of tetrahydrofuran (500 ml) and water (500 ml). Calcium hydroxide (1.14 mol, 84.5 g) was then added. The solution was stirred for three hr at room temperature and then for an additional seven hr at 70 C. The mixture was filtered using suction. The mother

\*To whom correspondence should be addressed.

## HOMOGENEOUS POLYGLYCEROL DODECYL ETHER

liquor was concentrated under reduced suction. The mother liquor was concentrated under reduced pressure and then extracted with ethyl acetate. The acetate layer was washed with saturated sodium chloride aqueous solution, dried with anhydrous sodium sulfate, filtered, concentrated under reduced pressure, and purified by distilling in vacuo and with a silica column using chloroform to give 190 g of epoxide, V. The compound, V, was reacted with sodium diglycerate using the same procedure described in the above section. The reaction mixture was extracted with chloroform, purified with a silica column twice, first chloroform/methanol (90/10) and then chloroform/methanol (93/7) as solvent, and 59 g (20% yield) of tetraglycerol dodecyl ether, VI, was obtained.

**Phase diagrams.** Various amounts of water, surfactant and dodecane were placed in test tubes with a Teflon sealed screw cap. The procedure of shaking the test tubes and then letting them stand was repeated in a thermostatted bath until the solutions reached equilibrium. The solubility regions were determined visually or by a differential scanning calorimeter (DSC) (Seiko, DSC-100).

**Structure of mesophases.** The structures of mesophases were determined using an optical microscope with polarized light (Olympus, BH-II). Lamellar and hexagonal phases were identified by comparing the textures with photomicrographs found in literature (5-7).

**Surface tension.** Measurements were made by the Wilhelmy method (Kyowa Science, ESB-IV).  $R_{12}G_n$  aqueous solutions were placed in jacketed dishes with water circulated through the jacket at 25 C, and the surface tension was measured with a platinum plate.

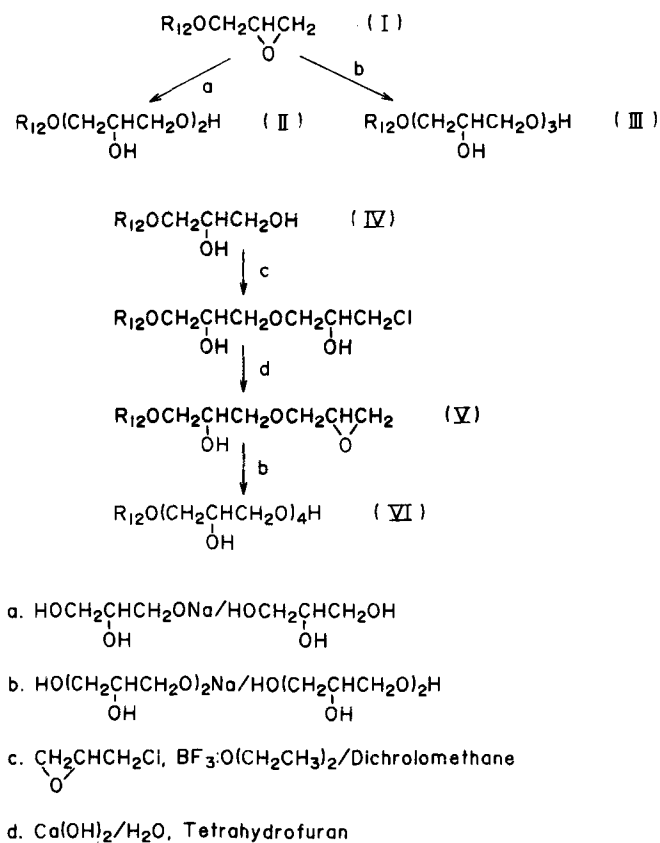


FIG. 1. Synthesis flow of  $R_{12}G_n$  ( $n = 2, 3$  and  $4$ ).

## RESULTS AND DISCUSSION

**Synthesis.** Figure 1 schematically shows the synthesis of polyglycerol dodecyl ethers II, III and VI. Their appearances, melting points, yields and analytical data are summarized in Table 1. The purity of the polyglycerol dodecyl ethers II, III and VI was determined by HPLC using a 7-C-18 column and aqueous acetonitrile in the mobile phase.

Proton magnetic resonance ( $^1H$ -NMR) spectra were obtained from samples of acetylated polyglycerol dodecyl ethers/carbon tetrachloride at 60 MHz with TMS as an internal lock. These surfactants included diastereoisomers derived from the polyglycerol chain, but were used without further purification.

**Phase diagrams of surfactant/water binary systems.** Figures 2-5 are binary phase diagrams of  $R_{12}G_n/H_2O$  ( $n = 1-4$ ) systems. The  $T_c$  curve shows the variation of the melting point of the surfactant with varying water fractions. The

TABLE 1

Analytical Data of  $R_{12}G_n$  ( $n = 2, 3$  and  $4$ )

	Appearance	Melting point (C)	Yield (%)	Purity <sup>a</sup> (%)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR <sup>b</sup> ( $\delta$ )
$R_{12}G_2$	Crystal	47-48	35	99.7	3475, 2925 1470, 1340 1120, 720	0.85(3H), 1.22(18H) 2.00(9H), 3.45(8H) 4.10(2H), 4.90(2H)
$R_{12}G_3$	Paste	—	38	93.4	3380, 2925 1475, 1340 1120, 720	0.90(3H), 1.30(21H) 2.02(13H), 3.5(11H) 4.10(2H), 5.00(2H)
$R_{12}G_4$	Paste	—	20	91.1	3360, 2925 1470, 1335 1120, 720	0.89(4H), 1.28(19H) 2.02(13H), 3.51(15H) 4.06(5H), 4.98(3H)

<sup>a</sup>HPLC

<sup>b</sup> $^1H$ -NMR of acetylated  $R_{12}G_n$ .

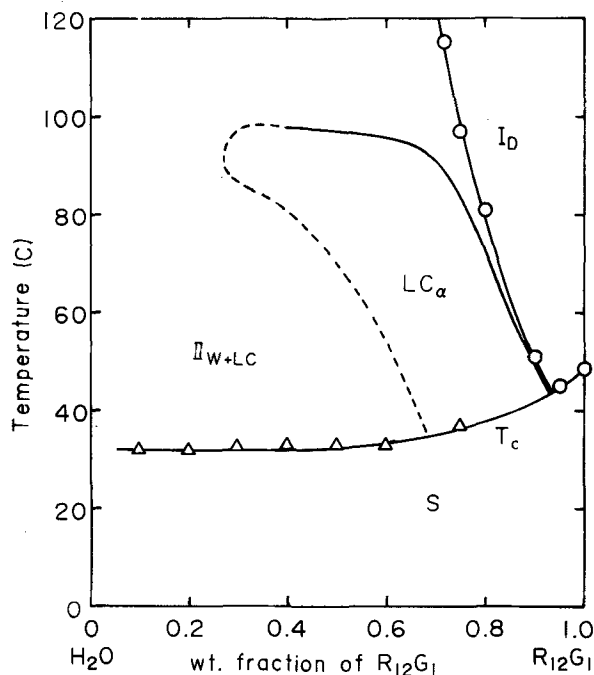


FIG. 2. Phase diagram of the  $R_{12}G_1/H_2O$  system. O, measurement by observation; A, measurement by DSC;  $I_D$ , isotropic surfactant solution;  $LC_\alpha$ , lamellar liquid crystal; S, solid;  $II_{W+LC}$ , water + liquid crystal.

values decrease with increasing water fractions. The shape of the  $T_c$  curve in nonionic surfactant/water systems is similar to that of other nonionic surfactant systems (8).

Liquid crystalline phases appeared adjacent to the  $I_D$  region. The characteristic patterns in the microscope with polarized light for these liquid crystalline phases are shown in Figure 6. The liquid crystals appearing in the  $R_{12}G_1$ ,  $R_{12}G_2$  and  $R_{12}G_3$  systems had a lamellar structure ( $LC_\alpha$ ).

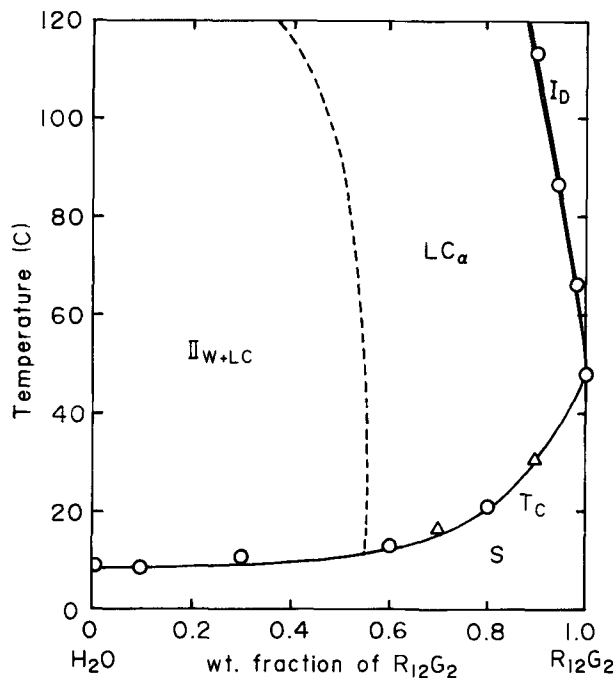


FIG. 3. Phase diagram of the  $R_{12}G_2/H_2O$  system.

The shape of the lamellar phase region for  $R_{12}G_1$  is similar to that for  $R_{12}EO_5$ . Although the lamellar phase for  $R_{12}EO_5$  changes to an aqueous solution and a hexagonal phase with decreasing temperature (8), neither an aqueous solution nor a hexagonal phase appeared in the system of  $R_{12}G_1$ . The lamellar phase for  $R_{12}G_2$  spread over the range of 20 to 120 C. Suzuki also showed that the lamellar phase was stable below 120 C in the diglycerol alkyl ether/water system (9). The upper temperature limits of the lamellar phase in the  $R_{12}EO_n/H_2O$  ( $n = 3-8$ ) systems are generally in the 60-70 C range (8). The stability of the lamellar phase at a higher temperature for  $R_{12}G_n$  suggests that the molecular association of  $R_{12}G_n$  is more stable than that of  $R_{12}EO_n$ . The liquid crystal appearing in the  $R_{12}G_4$  system had a hexagonal structure ( $LC_\beta$ ). The upper temperature limit of the  $LC_\beta$  region for  $R_{12}G_4$ , greater than 120 C, is higher than that for  $R_{12}EO_n$  ( $n = 5-8$ ). This result suggests that the solution behavior of  $R_{12}G_n$  is less temperature-dependent than that of  $R_{12}EO_n$ .

$R_{12}G_3$  was miscible in water. The isotropic surfactant solution continuously changed to an aqueous micellar solution with increasing water fraction. Water separated from the isotropic surfactant solution above a certain temperature, corresponding to cloud point. From Figures 4 and 7 (10), it can be seen the  $R_{12}EO_6$  system has almost the same cloud point as the  $R_{12}G_3$  system. Above the cloud point,  $R_{12}G_3$  retains more water than  $R_{12}EO_6$ . For example,  $R_{12}G_3$  retains 80 wt% of water at 100 C, whereas  $R_{12}EO_6$  retains only 25 wt% of water. Because a high water solubilization in non-aqueous solution (W/O microemulsion) occurs when the continuous phase changes from oil to surfactant, it is expected that  $R_{12}G_n$  has a stronger ability to solubilize water than  $R_{12}EO_n$ . A cloud point was not observed below 120 C in the phase diagram for  $R_{12}G_4$  (Fig. 5). The aqueous micellar solution,  $I_w$ , changed to the hexagonal liquid crystalline phase at about 50 wt% surfactant fraction. Temperature does not show a significant effect on the hexagonal phase

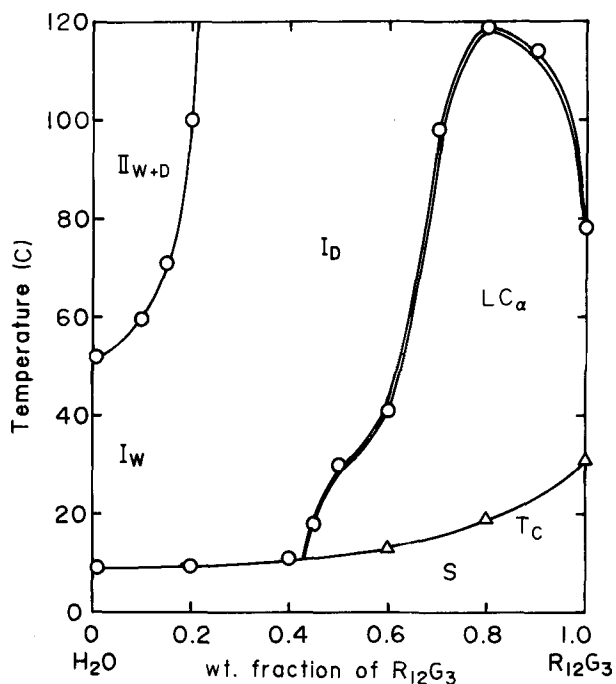


FIG. 4. Phase diagram of the  $R_{12}G_3/H_2O$  system.  $I_w$ , aqueous micellar solution;  $II_{W+D}$ , water + surfactant.

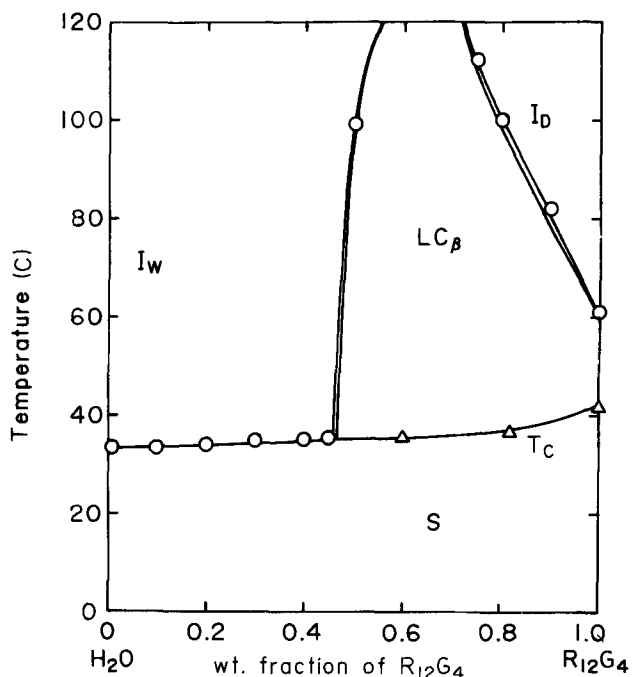


FIG. 5. Phase diagram of the  $R_{12}G_4/H_2O$  system.  $LC_\beta$ , hexagonal liquid crystal.

## HOMOGENEOUS POLYGLYCEROL DODECYL ETHER

region. There is no mesophase at high temperatures for the  $R_{12}EO_n$  systems (8). The hydration of the glycerol group may be significantly different from that of the ethylene oxide group at high temperature. In the  $R_{12}EO_n$  system, the composition at the  $I_W$  region boundary is more sensitive to temperature than in the  $R_{12}G_n$  systems. Between the  $R_{12}EO_4$  and the  $R_{12}EO_7$  systems, when ethylene oxide was increased by three units, the cloud point rose from 6 to 67 C (11). However, with an increase of one glycerol unit, the cloud point increased over 68 C between the  $R_{12}G_3$  and  $R_{12}G_4$  systems. This difference suggests that the hydrophilicity of the glycerol group is at least three times stronger than that of the ethylene oxide group, and that the hydration of the glycerol group is less sensitive to temperature than the hydration of the ethylene oxide group.

**Phase diagram of water/ $R_{12}G_2$ /dodecane.** The effect of temperature on the phase diagram of water/dodecane containing 3 wt% of  $R_{12}G_2$  was studied, and the result is shown in Figure 8.  $I_W$  (or  $I_O$ ) is a water-(or oil)-continuous solution. The solubilization regions for  $R_{12}G_2$  as a function of temperature are shown in order to compare its solubilizing power with that of  $R_{12}EO_6$  (Fig. 9). The solubilization of oil or water abruptly increased around the temperature at which the three-phase region appeared. Shinoda showed the hydrophile-lipophile tendency of nonionic surfactant systems changes from hydrophilic to lipophilic with increasing temperature (12,13).  $R_{12}G_2$  dissolves in the aqueous phase and forms a micellar solution ( $I_W$ ) at low temperature. This micellar solution ( $I_W$ ) continuously changes to the surfactant phase (O/W microemulsion) as more oil is solubilized. The hydrophilicity of the nonionic surfactant decreases with

increasing temperature, and a water phase separates from the O/W microemulsion at 48 C.  $R_{12}G_2$  dissolves in the oil phase and forms a reversed micellar solution ( $I_O$ ) at a high temperature. This reversed micellar solution changes to the surfactant phase (W/O microemulsion) when more water is solubilized. The solubility of oil in the surfactant phase decreases with decreasing temperature, and an oil phase separates from the surfactant phase at 73 C. A three-phase region of water/oil/surfactant appears in this temperature range (48-73 C). In this three-phase region, the type of emulsion inverts from O/W to W/O with increasing temperature. Shinoda termed this temperature the HLB temperature and showed that the HLB temperature has a linear relationship with the Griffin HLB value (13,14). Because  $R_{12}EO_6$  and  $R_{12}G_2$  have almost the same HLB temperature, the HLB value of  $R_{12}G_2$  is the same as that of  $R_{12}EO_6$ . The three-phase regions of the two systems appeared between 57 and 73 C. The solubilization of oil (or water) in aqueous (or oil) solution has a maximum peak at point A (or B) in Figures 8 and 9.  $R_{12}G_2$  solubilized 20 wt% of dodecane and 10 wt% of water, whereas  $R_{12}EO_6$  solubilized 5 wt% of dodecane and less than 1 wt% of water. Clearly, the surfactant phase of  $R_{12}G_2$  can solubilize more water (or oil) than that of  $R_{12}EO_6$ . The photographs in Figure 10 show the oil, water and surfactant phases in the three-phase regions for  $R_{12}G_2$  and  $R_{12}EO_6$ . The surfactant phase (middle layer) for  $R_{12}G_2$  has about four times as much volume as that of the  $R_{12}EO_6$  system. The aqueous (or oil) phase in Figure 10 is a surfactant mono-dispersed solution (15). The cmc of  $R_{12}G_2$  may be lower than that of  $R_{12}EO_6$  because of the smaller volume of the aqueous and oil phases.

**HLB values of  $R_{12}G_n$ .** The HLB values of  $R_{12}G_n$  were determined by phase inversion emulsification. This emulsification method was described in detail in the previous paper (16). The HLB values ranged from 4.0 ( $R_{12}G_1$ ) to 18.8 ( $R_{12}G_4$ ) (Fig. 11). The HLB values of commercial  $R_{12}EO_n$  were also plotted on the same figure because homogeneous  $R_{12}EO_n$  did not give any stable O/W emulsions. The finest O/W emulsion for the liquid paraffin/water system was obtained at HLB value = 11.2 by the combination of sorbitan

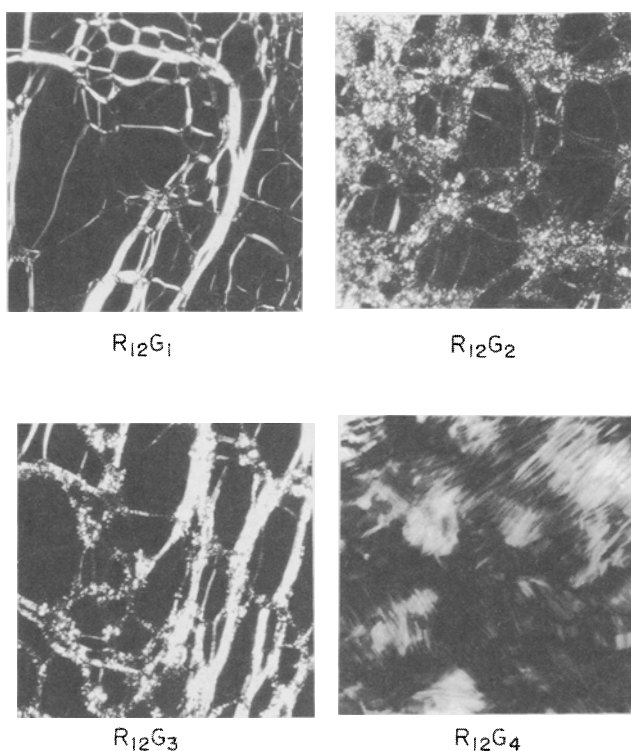


FIG. 6. Microscopy photographs in polarized light of the liquid crystals for the  $R_{12}G_n/H_2O$  systems ( $n = 1, 2, 3$  and  $4$ ).  $R_{12}G_n/H_2O = 70/30$  wt, 40 C.

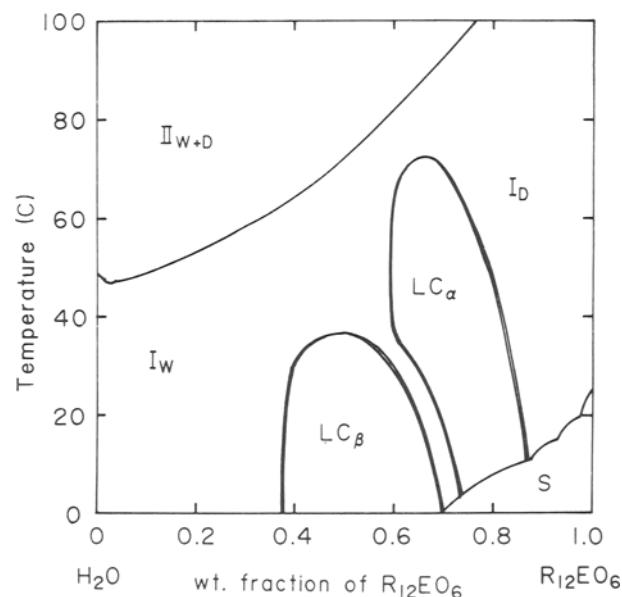


FIG. 7. Phase diagram of the  $R_{12}EO_6/H_2O$  system (9).

monostearate and polyoxyethylene (20) sorbitan monostearate. The HLB values of  $R_{12}G_n$  and  $R_{12}EO_n$  were calculated from the weight fraction of the combined surfactants with sorbitan monostearate (in this case the HLB values of  $R_{12}G_n$  and  $R_{12}EO_n$  are higher than 11.2) or polyoxyethylene (20) sorbitan monostearate (in this case the HLB values are lower than 11.2). Between  $R_{12}EO_6$  and  $R_{12}EO_9$ , an increase of three ethylene oxide units, the HLB value rose from 13.3 to

16.7. The HLB value increased from 13.0 to 16.3 between  $R_{12}G_2$  and  $R_{12}G_3$ , an increase of one glycerol unit. This result also shows that the hydrophilicity of the glycerol group is about three times stronger than that of the ethylene oxide group.

The emulsifying abilities of  $R_{12}G_n$  and  $R_{12}EO_n$  were compared using the average particle size of the O/W emulsions. The average particle size produced by  $R_{12}G_2$  was smaller than that of the emulsion produced by  $R_{12}EO_6$ . The particle distribution for  $R_{12}G_2$  was also narrower than that

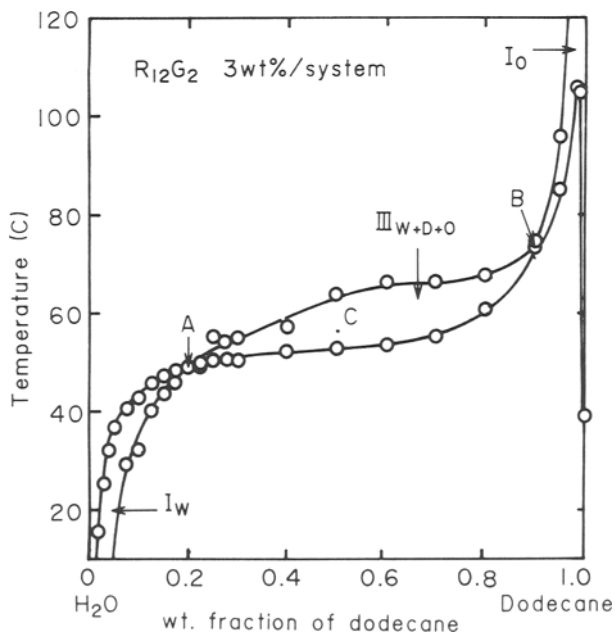


FIG. 8. Phase diagram of dodecane/ $H_2O$  system containing 3 wt% of  $R_{12}G_2$ . III<sub>W+D+O</sub>, water + surfactant + oil.

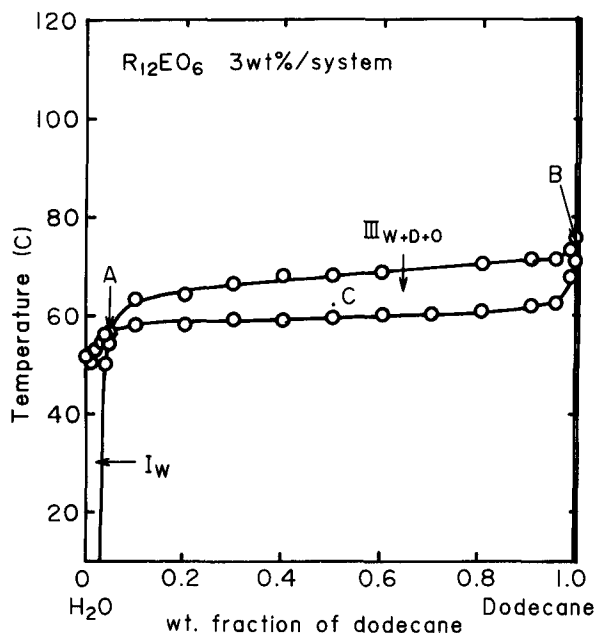


FIG. 9. Phase diagram of dodecane/ $H_2O$  system containing 3 wt% of  $R_{12}EO_6$ .

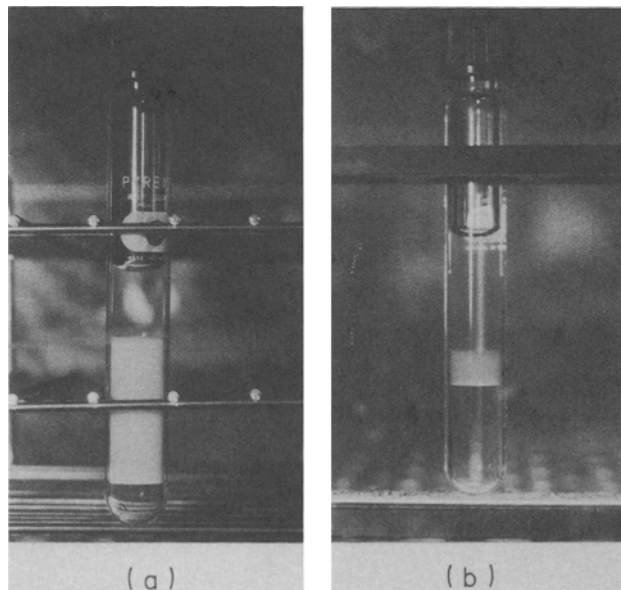


FIG. 10. Photographs of the three-phase regions for the  $R_{12}G_2$  system (a) and for  $R_{12}EO_6$  system (b). (a), Point C in Figure 6; (b), Point C in Figure 8.

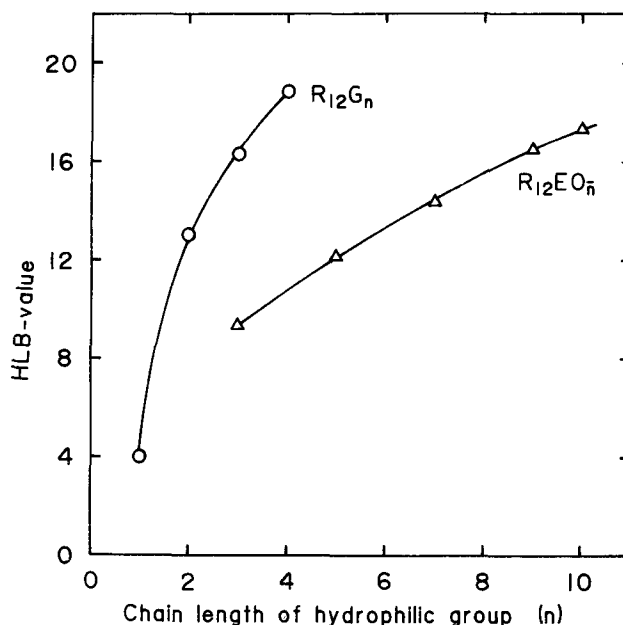


FIG. 11. HLB values of  $R_{12}G_n$  and  $R_{12}EO_n$ .

## HOMOGENEOUS POLYGLYCEROL DODECYL ETHER

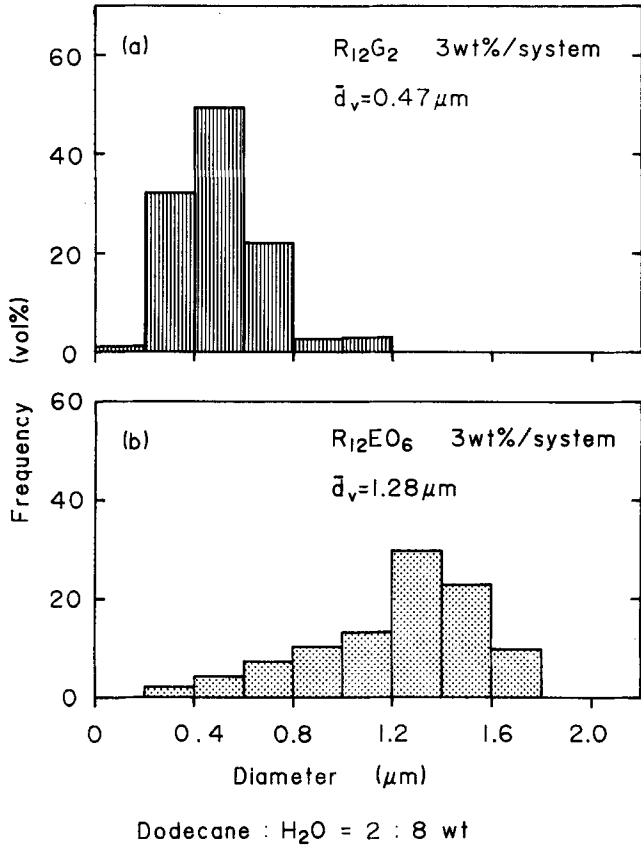


FIG. 12. Particle distribution of O/W emulsions prepared by  $R_{12}G_2$  (a) and  $R_{12}EO_6$  (b).

for  $R_{12}EO_6$  (Fig. 12). Because the HLB values of  $R_{12}G_2$  and  $R_{12}EO_6$  are almost the same, these results indicate that  $R_{12}G_2$  has a greater emulsifying ability than  $R_{12}EO_6$ . Fine emulsion is obtained in the range of low interfacial tension, and a low interfacial tension forms between surfactant and oil (or water) phases (17). The surfactant phase for  $R_{12}G_n$  expands to the low concentration region of the surfactant. This may be the reason why glycerol surfactants gave finer O/W emulsions than polyoxyethylene surfactants.

**Interface properties.** Surface tension ( $\gamma$ )-concentration plots (c) for  $R_{12}G_2$ ,  $R_{12}G_3$  and  $R_{12}EO_n$  ( $n = 5, 7$  and  $8$ ) (18) are shown in Figure 13. The cmc was taken as the concentrations at the point of intersection of the two linear portions of the  $\gamma$ -log  $c$  plots. Even though  $R_{12}G_2$  has higher hydrophilicity than  $R_{12}EO_5$ , the cmc and  $\gamma_{cmc}$  of  $R_{12}G_2$  are lower than those of  $R_{12}EO_5$ . This result reinforces the conclusion that the  $R_{12}G_n$  series associates more easily in aqueous media and has greater solubilizing and emulsifying abilities than the  $R_{12}EO_n$  series.

It is expected that emulsions produced with polyglycerol nonionic surfactants are more stable than those for the polyoxyethylene ones. However, there are still some problems. The product is more expensive than polyoxyethylene surfactants. Because the effect of one glycerol unit on the HLB is more sensitive, accurate control of the adducted glycerol number is required, but it is difficult to control the number for commercial products.

## ACKNOWLEDGMENT

The authors are grateful to K. Shinoda for valuable comments.

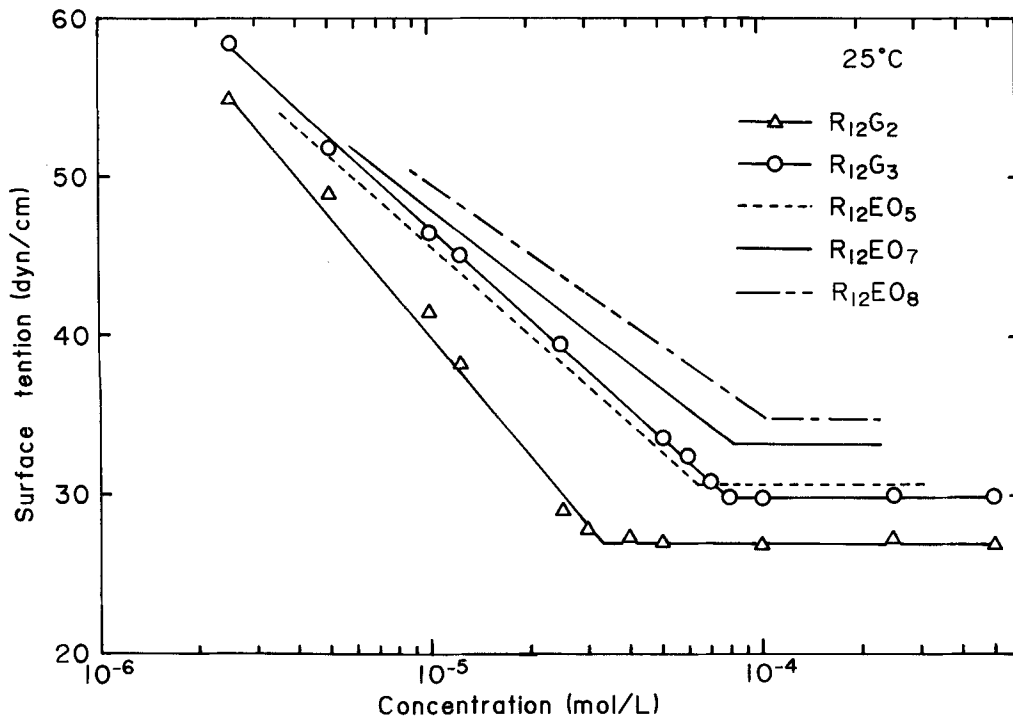


FIG. 13. Surface tension of the aqueous solutions of  $R_{12}G_n$  and  $R_{12}EO_n$  (18).

## REFERENCES

1. Babayan, V. K., T. G. Kaufman, H. Lehman and R. J. Tkaczak, *J. Soc. Cosmet. Sci.* 15:473 (1964).
2. Hemker, W., *J. Am. Oil Chem. Soc.* 58:114 (1981).
3. McIntyre, R. T., *Ibid.* 56:835A (1979).
4. Garti, N., and A. Aserin, *J. Liquid Chromatogr.* 4:1173(1981).
5. Rosevear, F. B., *J. Am. Oil Chem. Soc.* 31:628 (1954).
6. Moucharafieh, N., S. E. Friberg and D. W. Larsen, *Mol. Cryst. Liq. Cryst.* 53:189(1979).
7. Thundathil, R., J. O. Stoffer and S. E. Friberg, *J. Polym. Sci.* 18:2629(1980).
8. Mitchell, D. J., G. J. T. Tiddy, L. Waring, T. Bostock and M. P. McDonald, *J. Chem. Soc., Faraday Trans., I*, 79:975(1983).
9. Clunie, J. S., J. F. Goodman and P. C. Symons, *Trans. Faraday Soc.* 65:287(1969).
10. Suzuki, Y., and H. Tsutsumi, *J. Jpn. Oil Chem. Soc.* 36:947 (1987).
11. Mulley, B.A., in *Nonionic Surfactants*, edited by M. J. Schick, Marcel Dekker, New York, 1967, p. 430.
12. Nakagawa, T., and K. Shinoda, in *Solvent Properties of Surfactant Solutions*, edited by K. Shinoda, Marcel Dekker, New York, 1967, pp. 121-135.
13. Shinoda, K., and H. Saito, *J. Colloid Interface Sci.* 30:258 (1969).
14. Shinoda, K., H. Kunieda, T. Arai and H. Saijo, *J. Phys. Chem.* 88:5126(1984).
15. Harusawa, F., T. Saito, H. Nakajima and S. Fukushima, *J. Colloid Interface Sci.* 74:435 (1980).
16. Sagitani, H., *J. Am. Oil Chem. Soc.* 58:738 (1981).
17. Shinoda, K., and Y. Shibata, *Colloids Surfaces* 19:185(1986).
18. Rosen, M. J., A. W. Cohen, M. Pahanayake and X. Hua, *J. Phys. Chem.* 86:541(1982).

[Received March 15, 1988;  
accepted August 3, 1988]