Cloud and HLB Temperatures of Polyglycerol Didodecanoate Solutions

Hironobu KUNIEDA*1, Masaya KANEKO*1, Rika FUJIYAMA*1 and Masahiko ISHITANI*2

* 1 Graduate School of Environment and Information Sciences, Yokohama National University
   (Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, JAPAN)
* 2 Specialty Chemical Laboratory, Yokohama Research Center, Mitsubishi Chemical Co.
   (Kamoshida-cho, Aoba-ku, Yokohama 227-8502, JAPAN)

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Abstract: Effect of additives (inorganic salts and polyols) on the cloud point of water-polyglycerol didodecanoate ((C11)_2G_6) system was investigated as a function of the weight fraction of polyglycerol chain in whole surfactant, W_m/W_s, which is directly related to Griffin’s HLB number (= 20×W_m/W_s). The average number of dodecanoic acid residues attached to polyglycerol, m, is in the range of 1.6-2.3. Unlike an ordinary commercial polyglycerol surfactant, the surfactants used in this study contain a very small amount of unreacted polyglycerol. Compared with poly(oxyethylene)-type nonionic surfactant aqueous solutions, NaCl and Na_2SO_4 largely decrease the cloud point, whereas NaSCN and 1,3-butanediol abruptly increase it with increasing the salt concentration at a fixed W_m/W_s. However, in the absence of additive, the cloud point drastically increases with a small increase in the hydrophilic chain length or W_m/W_s. It means that the solubility of polyglycerol surfactant in water is not largely influenced by temperature but is highly dependent on W_m/W_s. The apparent large effect of additive on the cloud point is mainly attributed to the temperature-insensitiveness of the phase behavior of (C11)_2G_6. Single-phase or three-phase microemulsions are formed at the water/oil ratio = 1 in water/(C11)_2G_6/hydrocarbon (heptane, decane, hexadecane, and m-xylene) systems. As well as the cloud point, the three-phase temperature or HLB temperature is abruptly increased with a small increase in W_m/W_s. However, both W_m/W_s for the HLB temperatures are coincident around 25°C, since the hydrophilicity of polyglycerol chain per weight is almost similar to that of poly(oxyethylene) chain at room temperature. J. Oleo Sci., 51, 379-386 (2002).

Key words: polyglycerol didodecanoate, cloud point, microemulsion, three-phase behavior, HLB temperature

1 Introduction

Compared with conventional poly(oxyethylene)-type nonionic surfactants, polyglycerol fatty acid esters are bio-friendly surfactants, which are used for cosmetics, foods, pharmaceuticals, etc. Since polyglycerol surfactants are mixtures of complicated isomers and the surfactants usually contain a large portion of unreacted polyglycerols(1), the basic phase behavior and physico-chemical properties of the surfactants in solution have not been extensively studied at a basic level.

An aqueous solution of poly(oxyethylene)-type nonionic surfactant becomes cloudy, and phase separation known as so-called clouding phenomenon takes place with increasing temperature(2). Sagitani reported that the clouding phenomena of pure short-hydrophilic-chain polyglycerol alkyl ether solutions and the cloud temperatures abruptly increase with increasing the polyglycerol chain length(3). Recently, polyglycerol alkanoates with a narrow distribution of polyglycerol
chains were produced(4,5). Unreacted polyglycerol was also eliminated from the surfactants(5,6). The cloud temperatures of the purified polyglycerol didodecanoate solutions also increase abruptly with increasing the hydrophilic chain length as well as that in polyglycerol alkyl ether systems(7). This is, however, not because the phase behavior of polyglycerol surfactant is temperature-sensitive. The dissolution tendency of the polyglycerol surfactant is mainly dependent on its hydrophilic chain length in the homologues and the effect of temperature is not as large as that of poly(oxyethylene) surfactant. At lower temperatures like room temperature, \( W_m/W_e \) for the cloud points are almost the same for both poly(oxyethylene) and poly(glycerol) type surfactants, where \( W_m/W_e \) is the weight ratio of the hydrophilic chain to whole surfactant and is directly related to the classical Griffin’s HLB number(8). To be exact, \( 20 \times \frac{W_m}{W_e} \) is equal to the HLB number. \( W_m/W_e \) values for the clouding are very different at high temperature because the hydrophilicity of polyglycerol surfactant is not largely affected by temperature.

It is known that the cloud temperature is also affected by added inorganic salts or polylols. The order of effectiveness of added salts on “salting out” or “salting in” is called Hofmeister series. There are many studies on the effect of added salt on the cloud point in poly(oxyethylene) surfactant systems but a few in polyglycerol surfactant systems. Furthermore, although the change in cloud temperature was usually measured by changing salt concentration in previous papers, this method does not figure out the salt effect accurately because the effect of temperature on the hydrophilic-lipophile property of surfactant is very different depending on the type of the hydrophilic moiety.

In poly(oxyethylene) surfactant systems, emulsion type changes from O/W to W/O at particular temperature called PIT or HLB temperature, at which a bicontinuous microemulsion phase coexists with excess water and oil phases. The HLB temperature in poly(oxyethylene) surfactant has been extensively studied and the semi-empirical relation among HLB temperature, surfactant concentration, water/oil ratio, HLB number of surfactant are well established. Although it is reported that the HLB temperature appears in polyglycerol system, its dependence on the hydrophilic chain length has not been clarified.

In this context, we investigated the effect of added inorganic salts and polylols on the cloud point of purified polyglycerol didodecanoates in water. Effect of types of oils on the HLB temperature was also studied. The results are compared with poly(oxyethylene)-type nonionic surfactants.

2 Experimental

2.1 Materials

Polyglycerol dodecanoates \((C_{11})_mG_n\), with four different polyglycerol chain lengths, \((C_{11})_2G_{2,0}\), \((C_{11})_3G_{4,5}\), \((C_{11})_2G_{2,3}\), and \((C_{11})_2G_{10,7}\), and \((C_{11})_2G_{21,3}\), were supplied by Mitsubishi Chemical Corp. Pseudo-moving-bed chromatography was applied to obtain a narrow chain-length distribution of polyglycerols. The unreacted polyglycerol was removed by extraction method(5). The detailed procedures and the distribution of polyglycerol chains have been mentioned in our previous papers(4-6). The average number of dodecanoic acid per polyglycerol chain is indicated by m, the average polymerization degree of the hydrophilic chain is n. The contents of unreacted polyglycerol are 0.9% for \((C_{11})_2G_{2,0}\), 0.5% for \((C_{11})_2G_{4,2}\), 0.43% for \((C_{11})_2G_{7,3}\), 1.0% for \((C_{11})_2G_{10,7}\), and 2.1% for \((C_{11})_2G_{21,3}\), respectively. The polymerization degree of polyglycerol was obtained by the hydroxyl value measurement and the average number of alkanoic acid residue was calculated from the reaction ratio of polyglycerol/dodecanoic acid considering the amount of unreacted polyglycerol(6).

Since, approximately two dodecanoic acids are attached to one polyglycerol chain in the present surfactants, we call them polyglycerol didecanoates, \((C_{11})_2G_m\), \((C_{11})_2G_n\) with different hydrophilic chain length is a mixture of the above surfactants. Distilled water was used in the preparation of the samples.

Homogeneous poly(oxyethylene) dodecyl ethers \((C_{12}EO_n)\) were obtained from Nikko Chemicals Co.

2.2 Determination of Phase Diagram

Various amounts of water and surfactant were weighed and the mixtures were sealed in ampoules. Phase state and presence of liquid crystals were determined by direct visual inspection and by crossed polarizers, respectively.
3 Results and Discussion

3.1 Effect of Additive on the Cloud Temperature

The changes in cloud temperatures of C_{12}EO_{8} and (C_{11})_{2}G_{n} aqueous solutions were determined as a function of NaCl, Na_{2}SO_{4}, NaSCN, or 1, 3-butandiol concentration in water and the results are shown in Fig. 1. In order to adjust the cloud temperature of glycerol didodecaneoate solution equal to that of C_{12}EO_{8} solution in the absence of additive, we used a mixture of 96.4% of (C_{11})_{2}G_{13} and 3.6% of (C_{11})_{2}G_{10.7}. The weight fraction of the hydrophilic part in the total surfactant (W_{H}/W_{S}) is 0.587 for C_{12}EO_{8} and 0.578 for (C_{11})_{2}G_{n}. While calculating the molecular weight of hydrophilic part, the molecular weight of oxyethylene or glycerol unit is multiplied by the polymerization degree, and the end OH group and/or C=O group in the hydrophilic moieties are omitted. Then, 20 × W_{H}/W_{S} is coincident with Griffin’s HLB value.(8)

NaCl or Na_{2}SO_{4} decreases the cloud temperature whereas NaSCN or 1, 3-butandiol increases it in both surfactant systems. The extent of changing cloud temperature is much larger for polyglycerol surfactant than that for C_{12}EO_{8}. Hence, apparently, the additives largely influence the hydrophilicity of polyglycerol chain.

It was found, however, in our previous paper that the phase behavior of polyglycerol surfactant is temperature-insensitive compared with poly(oxyethylene) surfactant system and the cloud temperature abruptly increases with a slight increase in the polyglycerol chain length.(7) Hence, in order to analyze the additive effect, the difference in temperature dependence of surfactant phase behavior has to be considered.

3.2 Cloud Temperature as a Function of \( W_{H}/W_{S} \)

The change in cloud temperature of polyglycerol didodecaneoate aqueous solution as a function of \( W_{H}/W_{S} \) is shown in Figs. 2 and 3. The same experimental results for C_{12}EO_{8} solutions are also shown in the figures. The surfactant concentration in the system is kept at 3wt%. For polyglycerol surfactant, we used a mixture of each surfactant, whereas homogeneous C_{12}EO_{8} was employed.

In the case of poly(oxyethylene) type surfactants, it is known that the cloud temperature is almost same for surfactants having the same \( W_{H}/W_{S} \), even if the hydrophobic chain length is different(9). Hence, the \( W_{H}/W_{S} \) or Griffin’s HLB value is directly related to the cloud point. As is shown in Figs. 2 and 3, there is a linear relation between the cloud temperatures and \( W_{H}/W_{S} \) for C_{12}EO_{8} systems. Note that this linear relation does not hold at very high \( W_{H}/W_{S} \). (10)

In the absence of additive, the cloud point curve for polyglycerol surfactant is much steeper than that of C_{12}EO_{8} with increasing \( W_{H}/W_{S} \). This is in good agreement with homogenous polyglycerol dodecyl ether systems(3,7). If the cloud-point curve is completely vertical to the horizontal axis, the phase behavior is not influenced by temperature. In this case, the dissolution tendency is dictated only by the weight ratio of hydrophilic moiety to whole surfactant (\( W_{H}/W_{S} \)), and the cloud point phenomenon would never be observed. However, even in polyglycerol surfactant systems, the curve is slightly tilted, since the dipole-dipole interaction between water and the nonionic hydrophilic moiety is inversely proportional to temperature(11). In the case of poly(oxyethylene) surfactant, there is an additional factor to reduce the slope of cloud point curve in Fig. 2.
Fig. 2  Effect of Added Salt on the Cloud Temperature of 3 wt% Aqueous Solutions of $(C_{11})_2G_8$ (filled marks) and $C_{12}EO_8$ (open marks) as a function of $W_R/W_S$. a) NaCl, b) Na$_2$SO$_4$, c) NaSCN. The concentration of salt in water is 0 wt% (□), 5 wt% (■, ○) and 10 wt% (▲, △), respectively.

With increasing temperature, the conformation of poly(oxyethylene) chain is changed and the net dipole moment of hydrophilic moiety is decreased(12). This causes a dramatic decrease in hydrophilicity or hydration of poly(oxyethylene) chain. Hence, even at high $W_R/W_S$, the cloud point is observed. In fact, poly(oxyethylene) shows a cloud-point phenomenon without a lipophilic group when the molecular weight is large(10, 13). Per-
haps, there is no such drastic dehydration of polyglycerol chain in polyglycerol surfactant. As a result, the cloud point is abruptly increased with a small increase in hydrophilic chain in polyglycerol surfactant whereas the slope is very low in poly(oxyethylene) surfactant.

Both cloud-point curves for \((C_{11})_n G_n\) and \(C_{12}EO_n\) are intersected by each other around room temperature \((\sim 25^\circ\text{C})\), at which the interactions between water and hydrophilic moieties per weight or volume are almost similar for both surfactants in the absence of additive. In other words, Griffin’s HLB values to give a micellar solution are same at room temperature, but they are very different at high temperature. The abrupt increase in cloud temperature with a slight increase in polyglycerol chain does not mean that the glycerol unit is more hydrophilic than oxyethylene unit, but the hydrophilicity of the polyglycerol chain is only slightly changed with increasing temperature.

When salt or additive is added to the surfactant solutions, the cloud point curve is shifted to right-hand side with NaCl or Na\(_2\)SO\(_4\), whereas it is shifted to left-hand side with NaSCN or 1, 3-butanol. Cloud point curve breaks or is not smoothly connected to lower temperature on addition of NaSCN due to the formation of liquid crystal. At each temperature, the shift in the horizontal direction is larger in poly(oxyethylene) surfactant system than in polyglycerol surfactant system. It means that the hydrophilicity of poly(oxyethylene) surfactant is largely influenced by additives. The big change in cloud temperature of polyglycerol surfactant solution in Fig. 1 is attributed to the fact that the water-hydrophilic-chain interaction is not largely influenced by temperature, and the effect of additive on the change in hydrophilicity of the hydrophobic chain is lower for polyglycerol surfactant than for poly(oxyethylene) surfactant.

### 3.3 Three-phase Microemulsion

Although the phase behavior of polyglycerol surfactant is rather temperature-insensitive, the clouding phenomenon appears, as described before. Hence, it is possible that the surfactant phase behavior changes from water-soluble to oil soluble via a three-phase temperature in a water-oil system if an appropriate length of polyglycerol chain is carefully selected. Such a phase behavior is typically observed in poly(oxyethylene) surfactant systems, and the transition temperature is called HLB temperature or PIT at which the type of macroemulsion is also changed from O/W to W/O(14). Figure 4 shows a phase diagram of a water/(C\(_{11}\)_n G_n)/oil (decane or hexadecane) system as a function of temperature. The water/oil ratio is kept constant \((50/50)\), and the weight fraction of surfactant in the system \((X)\) is plotted horizontally.

The surfactant is dissolved in water and forms micelles at low temperature, whereas it forms a reverse micellar solution at high temperature. In between, macroemulsion of large solubilization is formed and it coexists with excess water and oil phases in a dilute region. Below the single-phase microemulsion, there is a region in which liquid crystal is present. Although the type of liquid crystal was not identified, lamellar liquid crystal may be dominant in the LCP region. The mid temperature of three-phase region and single-microemulsion + LCP region can be regarded as the HLB temperature(14). In a homogenous surfactant system, the three-phase region is usually parallel to the horizontal axis(14). In other words, the HLB temperature is independent of water/oil ratio or surfactant concentration. However, the three-phase region in the present system is skewed toward higher temperature. This is a typical phase behavior for a surfactant mixture(14,15). Although unreacted polyglycerols are removed from the
The HLB temperature increases because the three-phase behavior is mainly dictated by the nature of surfactant at the interface. We have to change the $W_n/W_s$ to form the three-phase microemulsion if oil is changed. If the $W_n/W_s$ is fixed and oil is changed, the three-phase region often disappears in polyglycerol surfactant systems.

### 3.4 Effect of Types of Oils on the HLB Temperature

The correlation between the HLB temperature and the HLB of polyglycerol surfactant ($W_n/W_s$) was studied. Figure 5 shows the phase diagrams of water/(C_{11})_2G_s/oil (heptane, decane, and hexadecane) systems as a function of $W_n/W_s$ of the surfactant. The water/oil weight ratio is unity. As is shown in Fig. 4, the HLB temperature (the middle temperature of three-phase region and single-microemulsion + LCP region) is dependent on surfactant concentration. However, at a relatively high surfactant concentration, the change is not large (15). Hence, the weight fraction of surfactant in the system is kept at 0.10 in Fig. 5. If the surfactant concentration is too high, the single-phase and LC-present regions are very wide and the HLB temperature cannot be determined accurately.

The HLB temperature is indicated by the broken curve which is located in the midst of three-phase region or single microemulsion + LC present region. On the left-hand side of the HLB-temperature curve, the surfactant mainly dissolves in oil whereas it forms aqueous micelles on the right-hand side. As well as the cloud temperature, the HLB temperature is very sensitive to $W_n/W_s$. In other words, the surfactant phase behavior is very temperature-insensitive compared with conventional poly(oxylethylene) surfactant. When the molecular weight of oil increases, the HLB temperature is shifted to low $W_n/W_s$. Namely, the HLB temperature rises with increasing the oil size if the surfactant is fixed as constant $W_n/W_s$. At high temperature, the solubilization of water and oil in the microemulsion decreases and a three-phase region appears. The monomeric solubility of nonionic surfactant in oil increases with increasing temperature. Therefore, the slope may be also increased due to the increase in the monomeric solubility as is discussed in the former section. It is, still, true that the HLB temperature is abruptly raised with increasing $W_n/W_s$, qualitatively.

In Fig. 6, the HLB curves for polyglycerol and poly...
Fig. 5  Effect of Temperature on Single-and Three-phase Microemulsion Region of \((C_{11})_2G_6\) as a Function of \(W_H/W_S\). (a) heptane, (b) decane, and (c) hexadecane. The surfactant concentration is 10 wt% in the system. II means a two-phase region consisting of two isotropic liquid phases. LCP is a region in which a liquid crystal is present.

(oxyethylene) surfactants are plotted against \(W_H/W_S\). The data for m-xylene are taken from our previous paper(7). The curves for these surfactants have very different slopes, but they are intersected around room temperature except in m-xylene system. Perhaps, in the m-xylene system, the monomeric solubility of surfactant in oil is high even at lower temperature. Since \(W_H/W_S\) is directly related to Griffin’s HLB value, the condition to
attain an optimum HLB in a given water-oil system is same for both surfactant systems. As well as the cloud point, this is because the water-hydrophilic-moiiety interaction per unit weight is almost the same at room temperature. It is clear from Fig. 6 that the temperature dependence of hydrophilicity of hydrophilic chain is very much different between two surfactants. In the poly(oxyethylene) surfactant system, when $W_H/W_S$ is fixed or the surfactant with a particular hydrophilic chain length is employed, the HLB temperature is shifted to higher temperature with increasing the molecular weight of oil or by changing aromatic hydrocarbon to saturated hydrocarbon. However, in the polyglycerol surfactant system, the apparent change in HLB temperature is so large that we have to adjust the $W_H/W_S$ to form a three-phase microemulsion in a different oil system.

4 Conclusions

Salts or polyols largely change the cloud temperature of aqueous polyglycerol didodecanoate solution compared with that of aqueous poly(oxyethylene) dodecyl ether solution. The phase behavior of the polyglycerol surfactant in water is rather temperature-insensitive, and the apparent large effect of additive on the cloud temperature is mainly attributed to the difference in temperature effect on the hydrophilic chain. The three-phase or HLB temperature of the polyglycerol surfactant in water-oil drastically increases with increasing the weight ratio of hydrophilic chain to whole surfactant ($W_H/W_S$). This is also attributed to the temperature-insensiveness of the polyglycerol chain. However, the $W_H/W_S$ for the cloud point and HLB temperature are almost the same around room temperature. It means that the hydrophilicity per weight of hydrophilic chain is same for polyglycerol and poly(oxyethylene) surfactants at room temperature.

References