Stability Conditions and Mechanism of Cream Soaps: Effect of Polyols

Hiromichi Sagitani and Masumi Komoriya *

POLA CHEMICAL INDUSTRIES, INC., 560 Kashio-cho, Totsuka-ku, Yokohama 244-0812 JAPAN

Abstract: Fatty acids, fatty acid potassium soaps, polyols and water are essential ingredients for producing stable cream soaps. The solution behavior of the above four components system has been studied to elucidate the effect of four sorts of polyols (glycerol, 1,3-butylene glycol, polyethylene glycol 400 and dipropylene glycol) on the stability of cream soaps. It has been revealed that the lamellar liquid crystalline one-phase converted to a two-phase of a lamellar phase and an isotropic aqueous solution by the addition of a few percent of 1,3-butylene glycol, polyethylene glycol 400 and dipropylene glycol, whereas the lamellar one-phase was remained by about 50 wt% of glycerol in the aqueous solution. The X-ray data at room temperature showed that the existence of 1:1 acid soap (1:1 mole ratio of potassium soap/fatty acid) crystals in the 1,3-butylene glycol, polyethylene glycol 400 and dipropylene glycol systems, whereas that the coexistence of 1:1 acid soap crystal and a lamellar gel phase (swelled lamellar gel structure) in the glycerol system. The phase transition peaks from coagel to gel (Tc) and from gel to liquid state (Tg) were appeared in the above four polyol systems by DSC measurements. It was confirmed from the combined data of SAXS and DSC that the existence of anhydrous 1:1 acid soap gels (or with small amount of bound water) in the all polyol systems, whereas the coexistence of the anhydrate gel and the swelled gel with a lot of intermediate water in the only glycerol system. This swelled gel structure would be contributed to stabilize the dispersed anhydrate acid soap crystals in cream soaps.

Key words: cream soaps, potassium acid soaps, polyols, phase diagram, SAXS, DSC, lamellar gel phase

1 INTRODUCTION

Cream soaps are used as facial cleansers in the personal care market and stability troubles such as phase separation and viscosity change often bother cosmetic formulation scientists. The stability conditions and mechanism of cream soaps by using the system of potassium acid soap-glycerol-water have been investigated in our previous work. The investigation elucidated that: i) cream soap is a dispersion system of 1:1 potassium acid soap (a complex of potassium soap and fatty acid at 1:1 molar ratio) in the lamellar gel phase; ii) glycerol aqueous solution is an crucial component for forming the lamellar gel phase. Many patents indicate that only glycerol is an essential polyol for forming stable cream soaps, even though various types of polyols are utilized as a moisturizer or a humectant in the personal care and cosmetic products. We aim to investigate in this study the reasons why only glycerol is used for the production of stable cream soaps in the above patents.

Many investigations have been carried out the effect of the addition of polyols on the gel formation in amphiphilic compounds/water systems. The melting temperature of the gel (Tc) decreases with the presence of 1,3-buthylene glycol and propylene glycol in the reports by Tomomasa and Van de Walle, whereas the additional effect of glycerol on Tc gives the different results in their studies. Tomomasa reported that Tc decreases with glycerol in the potassium stearate-water system, on the other hand Van de Walle showed that glycerol has no effect on Tc in the monoglyceride-water system. Baglioni et al. investigated the phase behavior of the vitamin C derived surfactants (alkanoyl-6-O-ascorbic acid esters)-water system. The critical micellization temperature (c.m.t) decreases significantly when propylene glycol and polyethylene glycol are added to the system. The c.m.t, however, increases slightly in the presence of glycerol. They concluded that the stabilizing effect of glycerol on gel would be due to the stabilization of the headgroup-solvent interactions rather than to an increment in film rigidity. They also considered that propylene glycol and polyethylene glycol can penetrate into the lopophilic layer at least partially from the decrease...
The phase diagrams of the surfactant-polyol aqueous solution systems will give us useful information to understand the phase behavior above $T_c$ and to estimate below $T_c$. Sagitani et al. investigated the existence of the gel phase, propylene glycol, 1,3-buthylene glycol, and polyethylene glycol on the structural change of the lamellar liquid crystalline phase above $T_c$. The interlayer spacing of the lamellar liquid crystals decreases with propylene glycol and 1,3-buthylene glycol concentration. On the other hand, polyethylene glycol and glycerol have no effect on the interlayer spacing. They considered that the existence site of glycerol would be between the headgroups of the lamellar liquid crystalline phase and that propylene glycol and 1,3-buthylene glycol could penetrate interlayer of hydrocarbon chain.

The formation of gel has been studied in the acid soap (1:1 potassium hydrogen oleate)-water system by Cistola et al. Two-phase region consisting of crystalline 1:1 acid soap and liquid water appears below $T_c$. A stable gel phase has not been reported in this 1:1 acid soap-water system. Kodama and Seki showed that the volume of “bound water” and “intermediate water” in the potassium stearate system was extremely less than that in the octadecyltrimethylammonium chloride and the dipalmitoyl phosphatidylcholine systems. Their results mean that octadecyltrimethylammonium chloride and dipalmitoyl phosphatidylcholine provide hydrated crystals and the stable gel phase, whereas potassium stearate gives an anhydrated crystal and the unstable gel phase. Zhu et al. carried out the structural studies in the triethanolamine acid soap-water system. The acid soap including water gives a lamellar liquid crystalline one phase at 80°C. The sample is a translucent gel on cooling to room temperature, over a few hours it turns white. Then the sample gradually separates into two phases. These data may show that the formation of practically stable lamellar gel phase is difficult over a few hours it turns white. Then the sample gradually gives a lamellar liquid crystalline one phase at 80°C. The formation of gel has been studied in the acid soap (1:1 potassium hydrogen oleate)-water system by Cistola et al. Two-phase region consisting of crystalline 1:1 acid soap and liquid water appears below $T_c$. A stable gel phase has not been reported in this 1:1 acid soap-water system. Kodama and Seki showed that the volume of “bound water” and “intermediate water” in the potassium stearate system was extremely less than that in the octadecyltrimethylammonium chloride and the dipalmitoyl phosphatidylcholine systems. Their results mean that octadecyltrimethylammonium chloride and dipalmitoyl phosphatidylcholine provide hydrated crystals and the stable gel phase, whereas potassium stearate gives an anhydrated crystal and the unstable gel phase. Zhu et al. carried out the structural studies in the triethanolamine acid soap-water system. The acid soap including water gives a lamellar liquid crystalline one phase at 80°C. The sample is a translucent gel on cooling to room temperature, over a few hours it turns white. Then the sample gradually separates into two phases. These data may show that the formation of practically stable lamellar gel phase is difficult without stabilizing agents.

There are many investigations regarding the gel formation of amphiphilic compounds/water systems or the effect of polyols on the gel transition temperature. However the additional effect of polyols on the formation of lamellar gel phase for stabilizing cream soaps has not been elucidated. We expect this work would give useful information for manufacturing stable cream soaps in the personal care industry.

2 EXPERIMENTAL

2.1 Materials

Myristic acid (purity: 98%) and glycerol (CH$_2$OH-CHOH-CH$_2$OH, purity: 99.8%) used in this investigation were obtained from Emery Oleochemicals, Singapore. Potassium hydroxide (purity: 85.0%) was purchased from Wako, Tokyo, and was used for the neutralization of myristic acid. Cosmetic grade of 1,3-buthylene glycol (CH$_2$OH-CH$_2$-CHOH-CH$_3$, Daicel, Osaka), di-propylene glycol (CH$_2$-CHOH-CH$_2$-O-CH$_2$-CHOH-CH$_3$, Asahi Glass, Tokyo), and polyethylene glycol 400 (HO-$(\text{CH}_2\text{-CH}_2\text{-O})_{10}$-H, PEG400, Toho Chemicals, Tokyo) were used without further purification. Water was deionized using an Organo FW-10 system.

2.2 Preparation of potassium hydrogen myristate

Potassium hydrogen myristate having different neutralization ratio were prepared by dissolving mixtures containing stoichiometric amounts of myristic acid and potassium hydroxide in anhydrous ethanol under a reflux condition. After crystallization of potassium hydrogen myristate at room temperature over a night, the solvent was removed by filtration. After evaporation of the solvent, the precipitate was dried several days at room temperature until weight was constant. Different neutralization ratio of 50, 55 and 60 mol% potassium hydrogen myristate was used for phase diagrams, SAXS and DCS. Because it was necessary to use an appropriate neutralization ratio or each measurement. Before the neutralization ratio was determined, it was confirmed that only lamellar liquid crystalline phase appeared above $T_c$ in such neutralization range (50-60 mol%)$^{13}$. It has been reported that acid soap crystal having 50 mol% of neutralization and soap crystal having 100 mol% coexist between the neutralization ratio of 50-100 mol% in potassium acid soap systems below $T_c$. Fifty mole percent (50 mol%) of neutralization (1:1 KHC$_{14}$) was selected for understanding the adding effect of polyols on the acid soap structure. On the other hand, more neutralized acid soaps were used for SAXS and DSC, because such combined acid soaps of 1:1 potassium acid soap and potassium soaps produced stable cream soaps$^{14}$. The purpose of this study is to understand the effect of the sort of polyols on the structure of acid soap gel, and to elucidate the stabilizing mechanism of cream soaps. It was possible to understand the relative effect of polyols on the structure of acid soap by different methods during the above neutralized range. An example of the abbreviation for the mixture of 0.5:0.5 mole potassium myristate and myristic acid will be shown as 1:1 KHC$_{14}$, hereunder.

2.3 Phase behavior diagrams

The mixtures of 1:1 KHC$_{14}$ and polyol were weighed and mixed by a vortex mixture in a glass bottle with a screw cap. And then water was added to the mixture. This procedure was useful for avoiding the formation of hard gel by soaps and water. The mixture was heated above the transition temperature ($T_c$) of the acid soap and cooled to below $T_c$ under a mixing condition. The phase behavior of the system of 1:1 KHC$_{14}$-polyol aqueous solutions was observed after several repeat of shaking and storage at various tem-
Stability Conditions and Mechanism of Cream Soaps: Effect of Polyols

J. Oleo Sci. 64, (8) 809-816 (2015)

Stability Conditions and Mechanism of Cream Soaps: Effect of Polyols

2.4 X-ray diffraction

A PANalytical, X’Pert PRO MPD with a small angle and a wide angle diffractometers was used to analyze the structural state of the solid phases with CuKα radiations (λ = 0.154 nm, 45 kV, 40 mA) at 25°C. The mixtures of 3:2 KHCl or 5:5:4.5 KHCl were used.

2.5 DSC measurement

Transition temperature from solid to liquid (Tc) and the calorimetric change (ΔH) at Tc were measured by a differential scanning calorimeter, SII DSC6000 at a scanning rate of 2°C/min. 5-15 mg of samples was placed in a sealed aluminum pan. The temperature was increased from 0 to 90°C and then decrease from 90 to −15°C. Tc by DSC was obtained from the peak temperatures on the heating curve and the cooling curve. Transition temperature from coagel to gel (Tgel) was determined from the peak temperature on the cooling curve. The mixtures of 1:1 KHCl or 3:2 KHCl were used.

3 RESULTS

3.1 Phase diagrams of the three-component system of 1:1 KHCl-water-polyol

The phase diagram of 1:1 KHCl-water-glycerol was shown in Fig. 1. The acid soap concentration in this system was fixed at 10 wt%, and the weight ratio of water and glycerol was varied from 0 to 100. The transition temperature (Tc) of hydrated 1:1 KHCl linearly increased from 42°C to 65°C when the concentration of glycerol increased in the aqueous solution. A lamellar liquid crystalline one-phase (LLC) obtained on the vertical axis of 100 wt% water remained until about 50 wt% of water was substituted for glycerol. The LLC changed to a two-phase region composed by an isotropic aqueous solution (W) and LLC at higher ratio of glycerol than 50 wt%. The optical anisotropy of the LLC gradually decreases with the concentration of glycerol in this two-phase region, and the LLC finally converted to an isotropic surfactant solution (D) at high glycerol concentration.

The phase diagrams of the 1,3-butylene glycol, PEG400 and dipropylene glycol systems are shown in Fig. 2, Fig. 3 and Fig. 4, respectively. Tc gradually decreased with the concentration of these three polyols. The increasing effect of the polyols on Tc was in the following order: 1,3-butylene glycol > glycerol > PEG400 > dipropylene glycol. Tc reached to 80°C in the 1,3-butylene glycol system, 65°C in glycerol, 61°C in PEG400 and 51°C in dipropylene glycol. The LLC appeared in the 1,3-butylene glycol, PEG400 and dipropylene glycol systems converted into a two-phase region of a lamellar liquid crystal and an isotropic aqueous solution (LLC + W) by the presence of a few percent of the polyols. The phase volume of LLC in the two-phase region gradually decreased with the concentration of the polyols and the two-phase region changed to an aqueous one-phase (W).

The HLB of acid soap will shift to more hydrophilic by the addition of 1,3-butylene glycol, di-propylene glycol and PEG400 since the solution changed from a lamellar phase to an isotropic aqueous phase. As a result, acid soaps would form micelles in the above three polyols systems. The HLB of acid soap in the glycerol aqueous solution has not a big effect with the concentration of glycerol.

Fig. 1 Phase diagram of the 1:1 KHCl-glycerol aqueous solution system.
LLC: Lamellar liquid crystalline phase, S: Solid, W: Aqueous solution.

Fig. 2 Phase diagram of the 1:1 KHCl-1,3-butylen glycol aqueous solution system.

J. Oleo Sci. 64, (8) 809-816 (2015)
The solution state of each phase appeared in Fig. 1, 2, 3 and 4, was determined from the change point of the temperature and the phase volume due to the change in composition, the optical anisotropy by polarized sheets and the solubility of each phase to polyol aqueous solutions. The mixture of 10 wt% 1:1 KHC<sub>14</sub> and 90 wt% water, left side point T<sub>c</sub>, was a liquid crystalline coloration one-phase exhibiting optical anisotropy above T<sub>c</sub>. This phase is confirmed to be a lamellar phase (LLC) in our previous work<sup>6</sup>. When the ratio of polyol to water increased, isotropic clear solution separated at the bottom of this LLC phase. This isotropic phase was thought to be a polyeol aqueous solution (W) from the coexistence with the LLC, the specific gravity of the isotropic solution to the LLC, and the solubility to water.

The phase volume of the LLC decreased with polyol concentration. Finally, the two-phase region (LLC + W) converted to an “aqueous one-phase” in Fig. 2, 3 and 4. In glycerol aqueous solution system, the two-phase region (LLC + W) remained at high concentration range of glycerol. With increasing glycerol ratio to water, the optical anisotropy of the upper layer decreased gradually and the LLC phase converted an isotropic solution. The lower phase (W) still existed with the isotropic upper phase at 100 wt% glycerol. Therefore, the upper phase was concluded to be an isotropic surfactant phase (D). An acid soap crystal (S) separated in all systems below T<sub>c</sub>, and two-phase region of S + W was formed.

### 3.2 X-ray diffraction

SAXS and WAXS measurements were carried out at room temperature (25°C) for understanding the structural change of acid soap in four types of polyol aqueous solutions. The SAXS profiles of the 50 wt% 3:2 KHC<sub>14</sub> and 50 wt% glycerol aqueous solutions were shown in Fig. 5. In the pure water system, the diffraction results showed the first, second and third order peaks at 2θ = 2.17, 4.37 and 6.58, respectively. This SAXS profile indicated a lamellar reflection of 1:2:1/3, and matched to the result of anhydrous 1:1 KHC<sub>14</sub> (2θ = 2.19, 4.39 and 6.59)<sup>6</sup>. The first order peak (A) height of the long spacing (2θ = 2.17) decreased with the concentration of glycerol, and a new broad peak (B) appeared in the smaller 2θ region as shown in Fig. 5. The SAXS profile obtained in the systems of KHC<sub>14</sub> and 1,3-butylene glycol aqueous solution showed no effect of the concentration of 1,3-butylene glycol (Fig. 6).

To compare the effect of the above-mentioned four polyols on the long spacing of the lamellar phases, the mixtures 50 wt% 3:2 KHC<sub>14</sub>, 20 wt% polyols and 30 wt% water were applied to SAXS measurements. The same lamellar profiles were obtained in the 1,3-butylene glycol, PEG 400 and dipropylene glycol aqueous solution systems as shown in Fig. 7. And only the glycerol system showed
Stability Conditions and Mechanism of Cream Soaps: Effect of Polyols

J. Oleo Sci. 64, (8) 809-816 (2015)

the different long spacing. The short spacing peaks of WAXS for $20^\circ \leq 20 \leq 25^\circ$ indicated the typical finger reflections\(^{14}\) in the all polyol systems (Fig. 8).

3.3 DSC measurement

Since it is difficult to obtain the information of phase behavior below $T_c$ by visual observation, DSC was used for understanding the phase transition information of the KHC\(_{14}\) and polyol aqueous solution mixtures. The peak profiles of $T_c$ in DSC heating and cooling curves in the 10 wt% 1:1 KHC\(_{14}\), 36 wt% polyols and 54 wt% water systems are shown in Fig. 9. The onset, peak and endset temperatures of the endothermic and exothermic peaks of Fig. 9 were summarized in Table 1. A sharp exothermic peak was obtained on the cooling curve of the 1,3-butylene glycol, PEG400 and dipropylene glycol systems. However, a broad exothermic peak was observed in the glycerol system. The temperature difference between endothermic and exothermic peaks of the glycerol system was higher than that of other polyol systems.

Since the phase transition temperature from coagel to gel ($T_{gel}$) was not identified in the 10 wt% KHC\(_{14}\) systems, the surfactant concentration was increased from 10 wt% to 50 wt%. A typical DSC heating and cooling curves of the 50 wt% 3:2 KHC\(_{14}\), 30 wt% water and 20 wt% PEG400 is

---

**Fig. 6** SAXS profiles of the acid soap systems composed by 60 wt% 5.5:4.5 KHC\(_{14}\) and 40 wt% of 1,3-butylene glycol aqueous solutions.

**Fig. 7** SAXS profiles of the acid soap systems composed by 50 wt% 1:1 KHC\(_{14}\), and 20 wt% polyols and 30 wt% water.

**Fig. 8** WAXS profiles of the acid soap systems composed by 50 wt% 1:1 KHC\(_{14}\), and 20 wt% polyols and 30 wt% water.

**Fig. 9** DSC peaks of the mixtures of 10wt% 1:1 KHC\(_{14}\), 36 wt% polyols and 54 wt% water.
shown in Fig. 10. The phase transition temperatures from coagel to gel ($T_{gel}$) and $T_c$ were observed at 9°C and at 50°C, respectively. $T_{gel,peak}$ and $T_{coagel,peak}$. On the exothermic curves in the four polyol systems were shown in Table 2, because only the exothermic peaks of $T_{gel}$ could be obtained in the all systems. $T_{gel,peak}$ appeared at almost the same temperature (8-9°C) in the all polyol systems.

**Table 1** Phase transition temperatures $T_c$ of the 1:1KHC$_{14}$-polyol aqueous solution systems.

|            | $T_{c,onset}$ | $T_{c,peak}$ | $T_{c,endset}$ | $T_{c,onset}$ | $T_{c,peak}$ | $T_{c,endset}$ | $\Delta T_{on-end}$ | $\Delta T_{c,peaks}$ | $\Delta T_{c,endset}$ |
|------------|---------------|---------------|----------------|---------------|---------------|----------------|----------------------|----------------------|----------------------|
| Glycerol   | 53.7          | 55.7          | 58.2           | 37.8          | 34.0          | 29.2          | 8.6                  | 15.9                 | 21.7                 | 29.0                 |
| 1,3-Butylene glycol | 53.4         | 56.8          | 59.4           | 50.4          | 49.4          | 46.6          | 3.8                  | 3.0                  | 7.4                  | 12.8                 |
| PEG400     | 51.7          | 55.3          | 57.8           | 46.9          | 45.4          | 42.7          | 4.2                  | 4.8                  | 9.9                  | 15.1                 |
| Dipropylene glycol | 43.2        | 47.7          | 50.0           | 41.0          | 38.8          | 36.5          | 4.5                  | 2.2                  | 8.9                  | 13.5                 |

*The sample composition is 10 wt% 1:1 KHC$_{14}$, 36 wt% water and 54 wt% polyol.

**Table 2** Phase transition temperatures, $T_c$ and $T_{gel}$ on the cooling curve of the 3:2 KHC$_{14}$-polyol aqueous solution systems.

|            | $T_{c,peak}$ | $T_{gel,peak}$ |
|------------|--------------|----------------|
| Glycerol   | 49.7         | 9.2            |
| 1,3-Butylene glycol | 50.3       | 8.3            |
| PEG400     | 50.0         | 8.1            |
| Dipropylene glycol | 44.8      | 8.7            |

*The sample composition is 50 wt% 3:2 KHC$_{14}$, 36 wt% water and 54 wt% polyol.

**4 DISCUSSION**

We elucidated in our previous study that stable cream soaps were formed in the lamellar gel phase composed by potassium hydrogen myristate, glycerol and water. The formation and the stability of cream soaps was be related to the solution behavior above $T_c$. The production of cream soaps carries out at heating conditions, and the storage temperature of the products sometimes goes up to 40-50°C. The solution behavior above $T_c$ of the mixtures of 1:1 KHC$_{14}$ and four types of polyol aqueous solutions shall be considered by using phase diagrams. A lamellar liquid crystalline one-phase is formed in the 10 wt% 1:1 KHC$_{14}$ and water system. The lamellar liquid crystalline phase remained at high concentration of glycerol. However, the lamellar one-phase easily converted to two-phase of a lamellar liquid crystalline phase and an isotropic aqueous solution (LLC+W) by the presence of a few percent of 1,3-butylene glycol, PEG400 and dipropylene glycol. In these three polyol systems, the existence of two phases of anhydrous 1:1 KHC$_{14}$ crystals and an isotropic micellar solution formed in the system of higher neutralized KHC$_{14}$ was considered from the both results of the phase diagrams and the X-ray diffractograms. The report by Kralchevsky supports that the coexistence of surfactant micelles and acid-soap crystallites in solutions of potassium myristate.

In the glycerol system, the coexistence of a swelled lamellar gel of KHC$_{14}$ and 1:1 KHC$_{14}$ crystals was assumed from the SAXS data. The molecules of 1,3-butylene glycol, PEG400 and dipropylene glycol would penetrate between the surfactant aggregation above $T_c$, and act as cosurfactants for forming micellar solutions. On the other hand, glycerol would strongly combine with the hydrophilic headgroups of the acid soaps. Therefore, the molecule would not penetrate into the hydrocarbon chains. The lamellar liquid crystalline one-phase would change to a lamellar gel phase retaining not only bound water but also intermediate water when the temperature goes down below $T_c$ in the glycerol systems. On the other hand, 1:1 acid soap crystals separate from the aqueous micellar solution below $T_c$ because the potassium hydrogen myristate an aqueous micellar solution with the 1,3-butylene glycol, PEG400 and dipropylene glycol.

The SAXS profiles appeared in the 1,3-butylene glycol,
PEG400 and dipropylene glycol systems matched to the structure of anhydrous 1:1 KHC\textsubscript{14}. There was no effect of the concentration of 1,3-butylene glycol, PEG 400 and dipropylene glycol on the long spacing. On the other hand, coexistence of anhydrous potassium acid soap and a new broad peak having longer interlayer spacing was obtained in the glycerol system. This broad peak would indicate that glycerol exists in the interlayer of the headgroup of acid soap and forms the swelled lamellar gel structure.

The WAXS data of the glycerol, 1,3-butylene glycol, PEG400 and dipropylene glycol systems show the no additional effect of polyols. These WAXS data show that the structure of the hydrocarbon chain part of KHC\textsubscript{14} has no effect of the concentration of the four types of polyols.

The DSC data show that there is a temperature region of the gel state between $T_{gel}$ and $T_{c}$ of in all polyol systems. From the SAXS and these DSC data, the existence of 1:1 KHC\textsubscript{14} crystals with a small amount of bound water and KHC\textsubscript{14} aqueous micellar solution is considered in the 1,3-butylene glycol, PEG400 and dipropylene glycol systems. There will be no intermediate water at the headgroup part of 1:1 KHC\textsubscript{14} in the 1,3-butylene glycol, PEG400 and dipropylene glycol aqueous solution systems, because Kodama and Seki showed that the bound water in the potassium fatty acid soap is extremely less than that in the cationic surfactant or amphoteric surfactant-water system\textsuperscript{10}. They also showed that the existence of intermediate water is not observed in the potassium stearate-water system by DSC measurements. The long spacing of the 3:2 KHC\textsubscript{14}-glycerol aqueous solutions shows the coexistence of 1:1 KHC\textsubscript{14} crystals with bound water and a swelled lamellar gel having a large amount of intermediate aqueous solution. The higher interaction between glycerol and the headgroups of fatty acid soaps will be a cause of the existence of the glycerol aqueous solution between the hydrophilic layers of potassium hydrogen myristate.

We would like to consider the foaming and cleansing ability of these polyol systems. The foaming ability was excellent within the neutralization range of 55-100 mol% in KHC\textsubscript{14}.\textsuperscript{6} It will be necessary to use more hydrophobic acid soaps for forming the lamellar gel in the 1,3-butylene glycol, di-propylene glycol or PEG 400 system. Because HLB of acid soaps shifts more hydrophilic by the addition of these three polyols. It would be not expected to get good foaming ability in these polyol systems when water was added to cream soaps during the cleansing process.

5 CONCLUSION

It was revealed the reasons why the glycerol aqueous solution is advantage to the 1,3-butylene glycol, PEG400 and dipropylene glycol aqueous solutions for the production of stable cream soaps from the phase diagrams, the X-ray diffractionometry and DSC measurements. Glycerol aqueous solution gives a wide range of LLC one-phase region, whereas the LLC phase converted into the two-phase region of LLC and an isotropic aqueous phase by the small amount of 1,3-butylene glycol, PEG400 and dipropylene glycol by the phase diagram observation. The LLC one-phase at the manufacturing temperature was necessary to produce stable cream soaps when the mixture was cooled down to the storage temperature. The LLC composed by acid soap and water was converted into a two-phase region of a micellar aqueous solution and 1:1 acid soap crystals, because there is no intermediate water in the potassium acid soap-water system. On the other hand, the lamellar gel phase having intermediate water is formed in the potassium acid soap-glycerol aqueous solution. It was assumed that a swelled lamellar gel is formed by the strong interaction of glycerol molecule with the headgroups of acid soaps. Cream soaps would have a dispersion structure of 1:1 acid soap crystals in the swelled lamellar gel phase. If we select some polyols forming the swelled lamellar gel like glycerol, stable cream soaps would be able to produce.

References

1) Fujiyama, M.; Yasumasa, T.; Nagai, K.; Fukuda, H. Creamy detergent composition. JP2002-154946(A).
2) Noguchi, Y.; Ohki, J.; Miyamoto, A. Face washing cream of fatty acid soap. JP2002-226359(A).
3) Tamura, T.; Wakita, K.; Ishida, M. Creamy detergent composition JP2010-209220(A).
4) Komorisono, M.; Oka, M. Creamy facial cleanser. JP2011-213693(A).
5) Kamiya, M.; Yoshida, M. Creamy detergent composition. JP2011-144488(A).
6) Sagitani, H. Stability conditions and mechanism of cream soaps: Role of glycerol. J. Oleo Sci. 63, 365-372 (2014).
7) Tomomasa, S.; Harusawa, F.; Machida Y. Phase transitions of the potassium stearate-water-polyol systems. J. Oils Chem. Soc. Jpn. (Yukagaku) 36, 938-942 (1987).
8) de Walle, D. V.; Goossens, P.; Dewettinck, K. Influence of the polarity of the water phase on the mesomorphic behaviour and the $\alpha$-gel stability of a commercial distilled monoglyceride. Food Res. Int. 41, 1020-1025 (2008).
9) Ambrosi, M.; Nostro, P. L.; Fratoni, L.; Dei, L.; Ninham, B. W.; Palma, S.; Manzo, R. H.; Allemandi, D.; Baglioni, P. Water of hydration in coagles, Phys. Chem. Chem. Phys. 6, 1401-1407 (2004).
10) Sagitani, H.; Ikeda, I.; Ohgo, Y. Effect of polyols on the association state of nonionic surfactants in aqueous solution: Utilization of polyols for increasing the solu-

---

**J. Oleo Sci.** 64, (8) 809-816 (2015)**
bilization of oil. *J. Oil Chem. Soc. Jpn. (Yukagaku)* **33**, 156-161 (1984).

11) Cistola, D. P.; Atkinson, D.; Hamilton, J. A.; Small, D. M. Phase behavior and bilayer propertied of fatty acids: hydrated 1:1 acid-soaps. *Biochemistry* **25**, 2804-2812 (1986).

12) Kodama, M.; Seki, S. Thermodynamical investigations on phase transitions of surfactant-water systems; thermodynamic stability of gel and coagel phases and the role of water molecules in their appearance. *Adv. Colloid Interface Sci.* **35** 1-30 (1991).

13) Zhu, S.; Pudney, P. D. A.; Heppenstall-Butler, M.; Butler, M. F.; Ferdinand, D.; Kirkland, M. Interaction of the acid soap of triethanolamine stearate and stearic acid with water. *J. Phys. Chem. B* **111**, 1016-1024 (2007).

14) Tandon, P.; Forster, G.; Neubert, R.; Wartewig, S. Phase transitions in oleic acid as studied by X-ray diffraction and FT-Raman spectroscopy. *J. Mol. Struct.* **524**, 201-215 (2000).

15) Kralchevsky, P. A.; Boneva, M. P.; Danov, K. D.; Ananthapadmanabhan, K. P.; Lips, A. Method for analysis of the composition of acid soaps by electrolytic conductivity measurements. *J. Colloid Interface Sci.* **327**, 169-179 (2008).

16) Boneva, M. P.; Danov, K. D.; Kralchevsky, P. A.; Kralchevksa, S. D.; Ananthapadmanabhan, K. P.; Lips, A. Coexistence of micelles and crystallites in solutions of potassium myristate: Soft matter vs. solid matter. *Colloid and Surfaces A* **354**, 172-187 (2010).