

The Formulation of Semi-Transparent Gel Emulsion by the Liquid Crystal Emulsification Method

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Abstract : Liquid crystals offer plenty of useful activities as improving the stability of emulsion, increasing moisturizing power, drug release, improving skin feeling and visual effect for cosmetics fields. In order to prepare stable semi-transparent gel emulsion, liquid crystal emulsification method was used. The emulsion stabilities of systems containing glycerin, fatty alcohols, surfactants, water and oil were investigated at various temperatures as time passed. The stabilities of all emulsions were evaluated by means of a polarizing microscope, SEM, rheometer, colorimeter and DSC. Even though the samples stored at 50°C thermostatic chamber were occurred the reduction of hardness, turbidity and ΔH and the peak shift, the semi-transparent gel emulsion was very stable without separation between water and oils phase in emulsion

Keywords : *Liquid crystal, Emulsion stability, Hardness, Turbidity, DSC*

1. Introduction

Liquid crystals are structures of intermediate state between the liquid and solid ones and lamellar structures were produced by the arrangements of organic molecules composed of hydrophilic and lipophilic component with multi-layers. In cosmetics and medicines fields, liquid crystals have applied for the formation of skin barriers, improvement of the stability of water-soluble or oil-soluble effective

components and a transmission media, because they have a similar structure of stratum corneum lipids. Therefore, liquid crystals offer plenty of useful activities for cosmetics fields. Liquid crystals are used for as follows in cosmetics industry.

- Improving stability of emulsion
- Controlling of rheological property
- Increasing moisturizing power
- Drug release
- Improving skin feeling
- Visual effect

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The formation of a liquid crystalline phase in an emulsion is influenced by the temperature[1–2], the type of oil[3], and the hydrophilic–lipophilic balance of the surfactant [4–6]. With respect to an O/W emulsion, it is known that fatty alcohols such as cetylalcohol and stearyl alcohol increase the viscosity of the emulsion and they also improve the stability of emulsion. The physico–chemical characteristics of fatty alcohols have been studied by researchers[7–10]. The balance of fatty alcohols and surfactant, in terms of their amount, was important of the formation of liquid crystals. Fatty alcohols have a thickening effect on emulsions, which is called self–bodying action. Barry studied the rheological properties of various emulsions which were stabilized by mixed emulsifiers of fatty alcohols and surfactants[11–13]. He concluded that the self–bodying action of fatty alcohols was caused by the formation of a network structure of liquid crystalline phase in the emulsion system. In a cosmetic o/w emulsion the lamellar structure is arranged around the oil droplets as concentric circles that are several layers thick. These layers are preventing the oil droplets from coalescence. Furthermore, the lamellar layers are surround–ing small groups of oil droplets called secondary droplets. These structures improve not only the stability but also water–retaining ability of emulsions[14–15]. (Fig. 1)

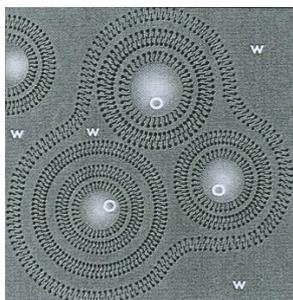


Fig. 1. Schematic presentation of secondary droplets

Liquid crystals have characteristics of intermediate state between the liquid and solid ones and possess a characteristic of anisotropy. The transition from isotropic to anisotropy can be observed by measuring X–ray diffraction, volumetric change, rheology, vapor pressure, NMR, calorimetry and microscopy. Also, liquid crystals have a characteristic of birefringence, this can be observed by a polarized microscope.

The goal of this study was to develop semi–transparent gel emulsion by liquid crystals emulsification method and to objectively evaluate the stabilities of this emulsion by instrumental analysis. Therefore, we are going to suggest an objective stability assessment method for liquid crystal.

2. Experimental

2.1. Materials

PEG–5 glyceryl stearate(Nihon Emulsion Co.) and C14–22 alcohol/C12–20 alkyl glucoside(Seppic) were used as non–ionic surfactants. Fatty alcohols were used cetyl alcohol, cetostearyl alcohol(cetyl alcohol : stearyl alcohol = 1:1) and stearyl alcohol. Cosmetic grade triethylhexanoin, 98% purity glycerin and deionized water were used.

2.2. Samples preparation

Table 1 shows the compositions of sample A1 and A3. Each sample was prepared as scheme I. T.K. Robomixer (MARK II Model 2.5) was applied for the preparation of samples. We choose the final sample on the basis of the emulsion stability, feeling and availability. The composition of sample B is shown in Table 2.

The sample B was prepared as scheme I. All samples were respectively stored in thermostatic chambers maintained at -15°C , 0°C , 25°C , 40°C and 50°C and measured the rheology and stability as time passed

Table 1. The compositions of sample A1 to A3

Ingredients	A1	A2	A3
PEG-5 glyceryl stearate	3.0	3.0	3.0
Glycerin	To 100	To 100	To 100
Deionized water	0~30	0~30	0~30
C14-22 alcohol/C12-20 alkylglucoside	3.0	3.0	3.0
Triethylhexanoin	9.5	9.5	9.5
Cetyl alcohol	0~5	-	-
Cetostearyl alcohol	-	0~5	-
Stearyl alcohol	-	-	0~5

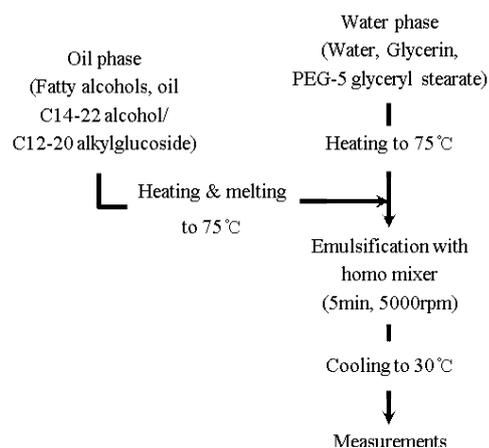
Table 2. The composition of sample B

Ingredients	B
PEG-5 glyceryl stearate	3.0
Glycerin	To 100
Deionized water	18.0
Triethylhexanoin	9.5
Stearyl alcohol	1.5
C14-22 alcohol/C12-20 alkylglucoside	3.0

2.3. Observations of the stability of emulsion

Optical microscopy experiment was performed by a polarizing microscope from Leica(DMRP, Germany) and SEM was performed by a Cryogenic scanning electron microscopy(Hitachi Co., S-4800).

The measurement of hardness was evaluated by a Fudoh Rheo Meter (RHEOTECH, RT-3005D) attached an adapter 15 ϕ in diameter(in condition of 2cm/min speed and 25mm depth). All samples were filled in a glass container and they were stored at various temperatures. They were evaluated the rheological properties and stabilities after stored at 25 $^{\circ}$ C for a day or a few months.



Scheme I. Sample preparation of A1, A2, A3 and B.

The turbidity was measured with a COH 300A model by Nippon Denshoku Corporation (Japan). The cell was produced by self-made using the slide and cover glasses.

DSC(differential scanning calorimetry) was used a 4100 DSC model by Calorimeter science Corporation. Heating rate was 1 $^{\circ}$ C/min from -15 $^{\circ}$ C to 80 $^{\circ}$ C. The area between peak and baseline was converted integral value to a thermal unit.

3. Results and Discussion

3.1. The region of liquid crystals

Fatty alcohols play an important role for the formation of liquid crystals with nonionic surfactants. In the emulsification system showed Table 1, the types and the amounts of fatty alcohols influence whether the formation of lamellar structure or not. It was found that the amounts of fatty alcohols affect the thickness of lamellar structure on a proportionate basis. But the stability of emulsion becomes worse, if the amounts of fatty alcohols increased overly.

Fig. 2 shows the region of liquid crystals against water content and the amounts of fatty alcohols. The results showed that the largest

region of liquid crystals was formed when stearyl alcohol was used in emulsion. Also, stearyl alcohol made more stable the emulsion than the others. On occasion of samples stored at 50°C chamber, sample A1 and A2 were unstable, but sample A3 contained stearyl alcohol was kept stable

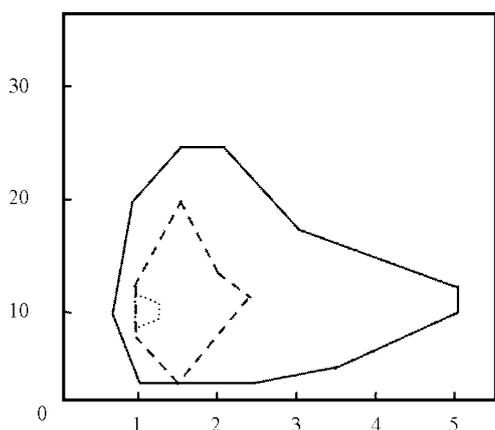


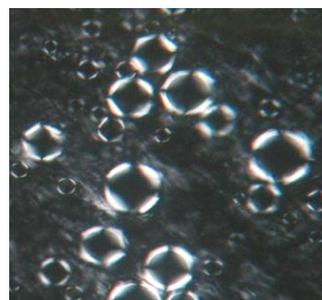
Fig. 2. The region of liquid crystal against water content and fatty alcohols wt% fraction concentration with samples of A1(.....), A2(---) and A3(—).

3.2. Observation with an optical microscopy

Liquid crystals have characteristics of intermediate state between liquid and solid ones and possess a characteristic of anisotropy. The transition from isotropic to anisotropy can be observed by many instrumental analyses. A polarized microscopy is the simplest analytical method among instrumental analysis. In Fig. 3, photographs obtained with sample B after storage at 25°C for 3 days were showed. As shown, the malteses cross could be clearly observed by a polarized microscopy and the interface is thicker than general O/W emulsion by the formation of liquid crystals.



(a)



(b)

Fig. 3. Photographs obtained with sample of B after storage at 25°C for 3 days. (a) without polarized light (b) under polarized light. Magnification×400.

In Fig. 4, Multilamellar structures were observed by SEM and the particle sizes of drops were about 5~10 μm.

The stabilities of sample B were evaluated at various temperatures. First of all, we observed the liquid crystals with the microscopy whether the sample B has kept liquid crystals structures as time passed. The results of observation after storing for a month and three months at various temperatures were shown in Fig. 5.

Liquid crystals structures have stably maintained at various temperatures as time passed, specially, the liquid crystals structures of the sample stored at 50°C was observed thicker than the ones stored at other temperature. This phenomenon will be discussed later.

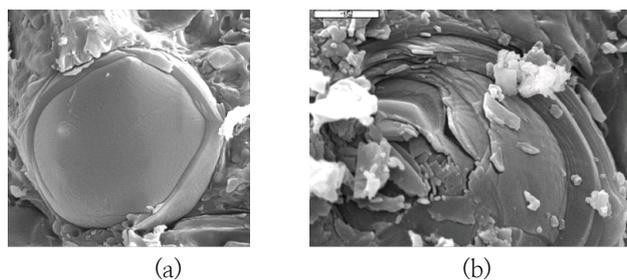


Fig. 4. Cryogenic scanning electron micrographs obtained by freezing, fracturing and coating the sample of B. (a) Magnification \times 3,000 (b) Magnification \times 5,000.

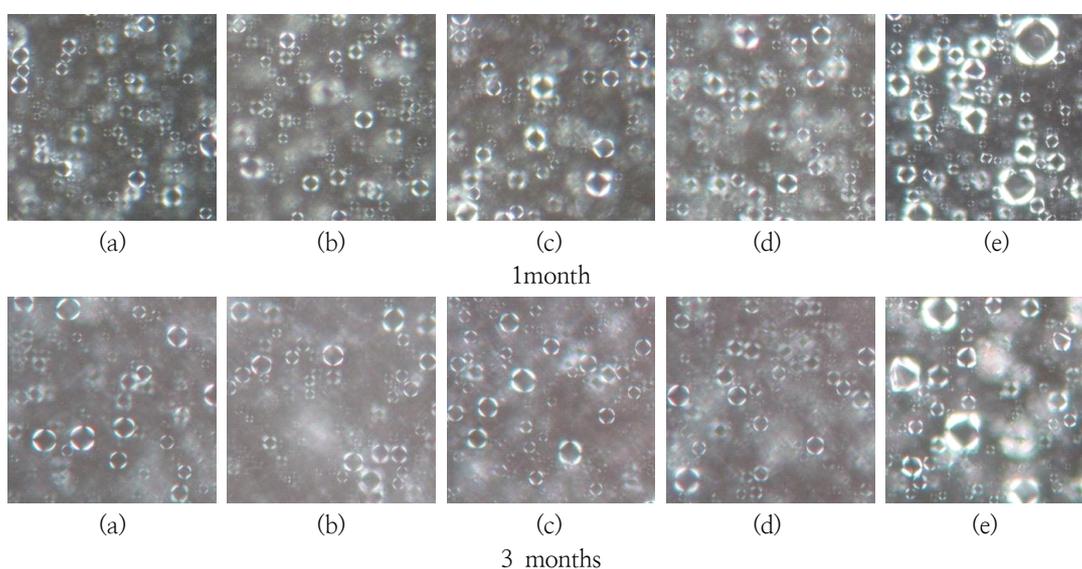


Fig. 5. Photographs obtained under polarized light with sample of B after storage at 25°C(a), -15°C(b), 0°C(c), 40°C(d) and 50°C(e) for stated times. Magnification \times 400.

3.3. Observation of the changes of hardness

The hardness of sample B was measured by a Fudoh Rheo Meter. Before measuring the hardness of samples, the ones had stored at various temperatures were maintained in thermostatic chamber at 25°C for a day. As shown in Fig. 6, the hardness of samples stored at below 40°C was very stable without the change as time passed, but the hardness of sample stored at 50°C was reduced after a certain time.

The hardness of sample B was decreased

over 48°C enough to cause flow. Therefore, if it was stored at 50°C for a long time, the mass transfer rearranged with organic molecules in emulsion could be happened and this is able to one cause of the hardness reduction. Although the hardness of sample stored at 50°C was decreased, there was observed no separation between water and oil phase in emulsion.

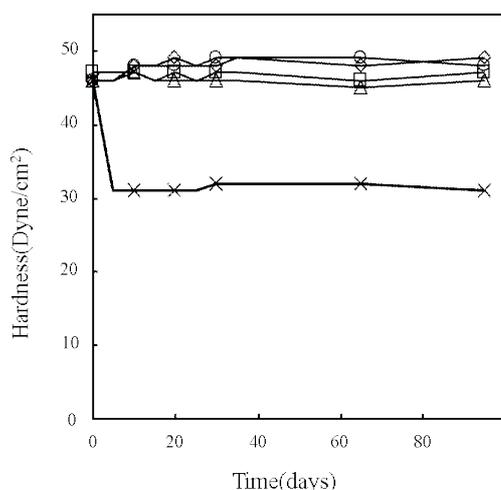


Fig. 6. Hardness changes of B sample during storage at 25°C(\diamond), -15°C(\square), 0°C(\circ), 40°C(\triangle) and 50°C(X).

3.4. Observation of turbidity

The turbidity of samples stored at various temperatures was measured for the evaluation of stability. If there were the phenomena such as agglomeration, coagulation and flocculation, the turbidity of emulsion was increased. It is reasonable conclude that the samples stored at various temperature were stable when we could not find any difference of the turbidity among samples as time passed.

The colorimeter(COH 300A, Nippon Denshoku Inc. Co., Japan) was used for the measurement of turbidity. The cell included in this equipment was barely suitable for the turbidity of sample B because the cell thickness is too thick to measure the turbidity. So we measured the turbidity of sample B with the cell produced by self-made as Fig. 7. We reduced the cell thickness so that light can pass through.

This cell device was easily fabricated using slide and cover glasses. The turbidity was measured with samples stored at various temperatures (-15~50°C) for a month, and just one day before the checking day, the samples were stored in thermostatic chamber maintained at 25°C. The thickness of the light

passing through the samples was fixed at 0.3mm

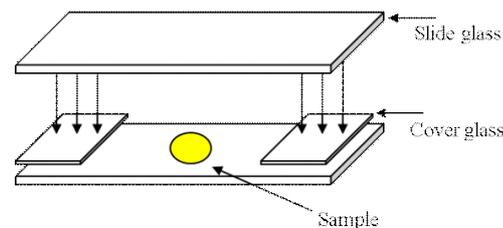


Fig. 7. A cell device for measuring turbidity by self-made.

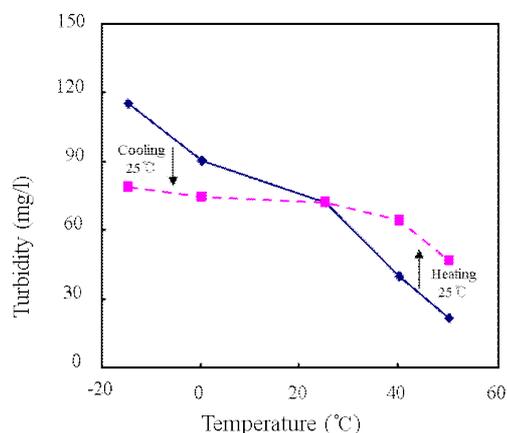


Fig. 8. Turbidity change of B sample as Temperature(Thickness 0.3mm).

Fig. 8 shows the turbidity change of samples at various temperatures. The turbidity is in inverse proportion to temperature. It is a natural consequence because when the temperature is low, the solubility of the surfactants and fatty alcohols in oils was decreased, as a result they was arranged at the interface more and that increases the turbidity and hardness. In case of the sample stored at 50°C chamber, the mass transfer in emulsion brings about as a result not fully recovered the turbidity in comparison with the others after it was stored at 25°C chamber for a day.

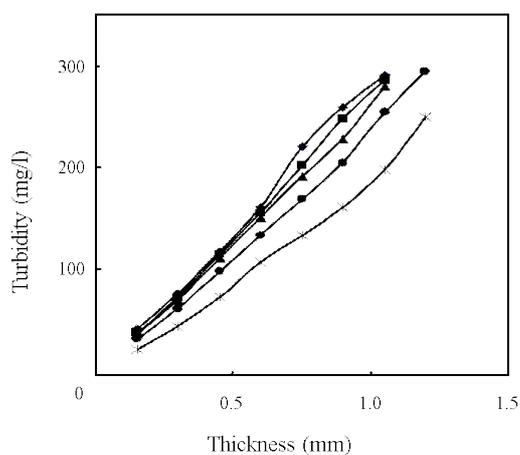


Fig. 9. Turbidity of B sample after storage at -15°C (◆), 0°C (■), 25°C (▲), 40°C (●) and 50°C (○) for a month.

Fig. 9 is shown the turbidity changes with sample thickness and temperature. The thickness of the light passing through the samples was increased with overlapping a cover glass (thickness 0.15 mm). The measurement methods were same as above and they were summarized as the average value after measuring three times per sample. The turbidity is proportional to the sample thickness. Same as above, in case of the sample stored at 50°C chamber, it makes a little difference in comparison with the others.

3.5. Observation with DSC

Differential scanning calorimetry or DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic.

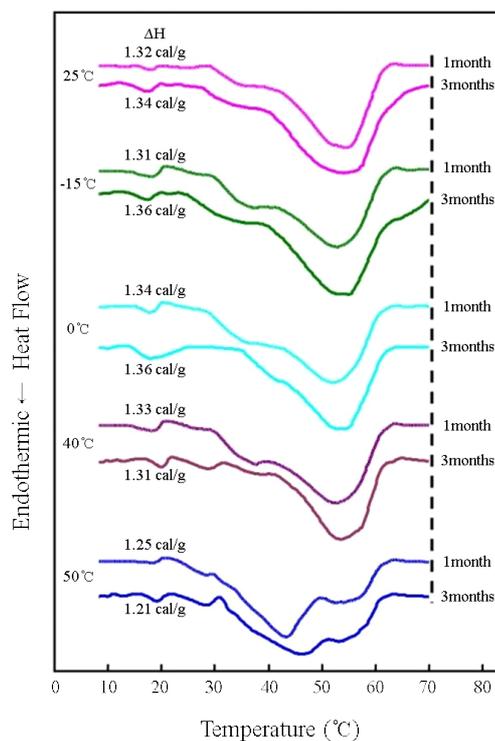


Fig. 10. DSC thermal profiles of sample B after storage at 25°C , -15°C , 0°C , 40°C and 50°C for stated times. Heating rate $1^{\circ}\text{C}/\text{min}$.

The thermal profiles of sample B were measured by DSC and they were observed by comparing with the samples stored in different conditions. Generally, we supposed that the sample stored at 25°C near room temperature is the most stable than the others. Therefore, we compared the graphs and ΔH between this sample and the others. Fig. 10 shows the thermal profile of the samples stored at various temperatures for a month and three months.

As shown in Fig. 10, the graphs and ΔH of the samples stored at below 40°C were similarly observed to each other. In case of the sample stored at 50°C chamber, the mass transfer in emulsion brings about the results as the peak shift and the reduction of ΔH . These results should be guessed the following

reasons. The samples were stored at higher temperature for a long period time and the organic molecules coordinated away from each other in multi-lamellar layers. Therefore, the peak moved toward low temperature and ΔH was slightly decreased. The photographs in Fig. 5, the multi-lamellar layers of the sample stored at 50°C chamber were observed thicker than the others. This is also the same reasons as mentioned above.

4. Conclusion

Semitransparent gel emulsions with distinctive appearances and characteristics were produced using a liquid crystal emulsification method, and the stabilities of the gels were determined. The formulations consisted of surfactants, glycerin, fatty alcohols, oil, and water. Stearyl alcohol generated the largest region of liquid crystals in the emulsion system. Generally, a formulation comprising a mixed cetyl and stearyl alcohol system is more effective for liquid crystal and stable emulsion formation than are systems using either alcohol in isolation. The results described above are ascribed to the use of a surfactant (C14-22 alcohols/C12-20 alkyl glucosides) that included fatty alcohols.

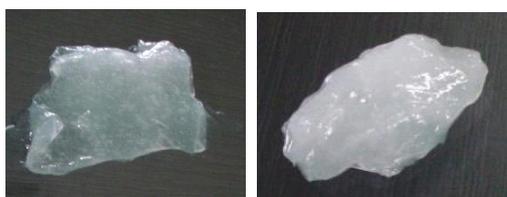


Fig. 11. Photographs of semi-transparent gel emulsion by the liquid crystal emulsification method.

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