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제미니형 계면활성제를 사용한 액정기술의 제조방법

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Preparation of Liquid Crystalline with Gemini Surfactant

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요 약: 제미니형 계면활성제를 사용하여 액정을 제조하였으며 보습효능을 측정하였다. 계면활성제로는 디코코일에틸렌디아민(PEG) -15설페이트 (SCD-PEG-15S) 3.0 wt%와 부스터로는 수소첨가 다이머에씨드에스터(HDAE) 4.0 wt%를 사용하였다. 안정화제로 베헤닐알코올(BA) 2.0 wt%와 리소레시친(LyL) 1.0 wt%를 사용하였다. pH 4.0~10.5 범위에서 안정하였으며 최적조건은 6.5이었다. 가장 안정한 상태의 점도는 8,000±500 cP이었으며. 입자크기는 4.0에서 15.5 μm 범위에서 가장 잘 형성되었다. 입자의 모양과 구조는 편광현미경을 통하여 관찰하였으며, LC의 입자 주변에 액정이 형성되었음을 확인하였다. 또한 액정의 입자주변에 겔 네트워크 구조를 형성하고 있다는 것을 알 수 있었다. 시료도포 후 30 min 경과후의 보습효과는 control보다 13.6% (*P<0.05) 증가함을 보였으며, 1 h 후의 보습효과는 control보다 12.6% (*P<0.05) 증가함을 보였다. 또한 4 h 후의 보습효과는 control보다 28.3% (*P<0.05) 증가하였다. 이는 제조한 액정이 라멜라형 구조를 형성하여 수분 포접력과 오일의 흡착력 증가로 인한 효과로 판단된다. 향후 피부의 전달체계(delivery system)에의 적용이 가능하고 나아가 의약이나 제약, 화장품 등을 만드는데 응용될 것으로 기대된다.

Abstract: In this study, liquid crystalline (LC) is formed using Gemini surfactant (GS) type and moisturizing effect *in vivo* is measured. 3.0 wt% of sodium dicocoyl ethylene diamine (PEG)-15 sulfate (SCD-PEG-15S) is used as GS and 4.0 wt% of hydrogenated dimer acid esters (HDAE) as booster. For stabilizers, 2.0 wt% of behenyl alcohol (BA) and 1.0 wt% of lyso-lecithin (LyL) are utilized. It is stabilized in pH from 4.0 to 10.5 and the best condition is in pH 6.5. The value of viscosity is 8,000 ± 500 cP. The most excellent particles are formed within the range of 4.0 to 15.5 μm. Formed LC is observed around LC particles using polarization microscope. It is also observed that lamellar gel network structure is formed around LC particles. Moisturizing effect is improved by 13.6% (*P<0.05) compared to control when measured 30 min later after coating samples. After 1 h, moisturizing effect is improved by 12.6% (*P< 0.05) than control while showing 28.3% (*P< 0.05) of improvement after 4 h. These results may be caused from that manufactured LC forms lamellar structure so that it has better water-holding ability and absorbance of oil increases. This formula could be utilized by delivery system (DS) on skin so that this technology can be applied for manufactuing pharmaceuticals and cosmetics.

Keywords: *liquid crystalline, moisture, Gemini surfactants, multi-layer, gel network structure*

1. Introduction

Liquid crystalline may exist between solid and liquid states. Precisely, although molecular arrangement with crystallization is not regular, regular state is known as liquid crystalline or meso-phase when compare with liquid[1]. Technology of liquid crystalline in cosmetics industry is using to improve stability of effective ingredient[2]. This liquid crystalline is method that improves O/W (oil-in-water) emulsion's stability, that is already proved, and it has been using cetyl alcohol and stearyl alcohol[3]. Suzuki[4] applied emulsion to cosmetics introducing liquid crystalline theory by method that supply suitable oil and water in skin. But, there is

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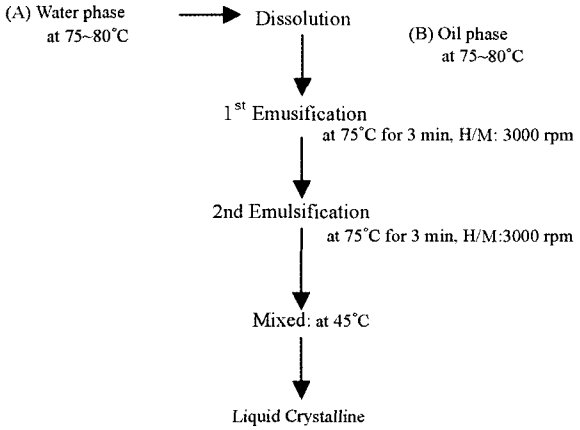

Figure 1. Manufacturing method of LC with Gemini surfactant in o/w emulsion.

shortcoming that preservation of stability and hardness of command drop in not equilibrium system a lot of studies and experiments have been proceed to solve this. Fatty alcohol of cetanol and stearyl alcohol concerned to O/W emulsion improves emulsification stability, and it was informed that do function that increase viscosity of system, and several kind of fatty alcohols are used in a lot of emulsification systems[5,6]. Nakanishi[7] compounds ingredient that is composing intercellular lipid properly and succeeded though moisture effect of skin makes excellent liquid crystalline. This liposome can speak that it is different but similar state with liquid crystalline as multi-lamellar structure's vesicles that differs with liquid crystalline. Thus, about liquid crystal, a lot of studies proceeded in various cosmetic industry fields[8-10].

Recently, Kim[11] succeeded to make liquid crystalline to use hydrogenated lecithin (HL). He succeeded to form liquid crystalline to use HL without using other emulsifiers. Also, Kim[12] encapsulated pro-vitamin B5 within liquid crystalline that is made using HL. And he succeeded to make O/W emulsion that have moisturizing effect. This technology developed by a more developed liquid crystalline technology[13-16].

In this study, it studied about a manufacture technology that makes O/W emulsion to use GS, and liquid crystalline of very transparent and small vesicle of multi-layer inside in this emulsion. To make liquid crystalline, used GS is SCD-PEG-15S. To make optimum liquid crystalline to use GS, experimented about condition of pH, slight effect, size of particle, effect of an

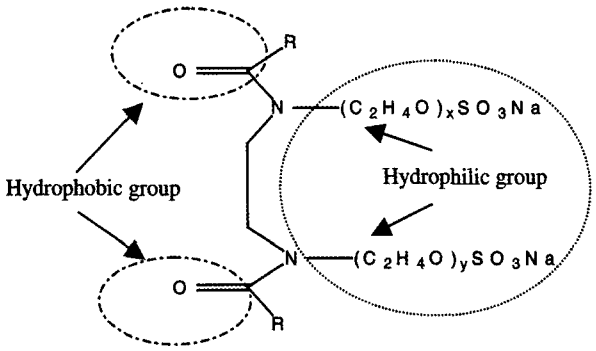

Figure 2. Molecular structure of Gemini surfactant; INCI: sodium dicocoylethylenediamine (PEG)-15 sulfate.

emulsifier etc. As condition to make liquid crystalline, it experimented about condition of pH, viscosity of particle, effect of an emulsifier etc. About the most excellent liquid crystalline, they observed formation availability of liquid crystalline through polarization microscope. Also, moisturizing effect makes superior essence product and measured skin moisturizing effect by passage time. The skin moisturizing effect reports result that did to women of arrested 20~30 ages and tests.

2. Experiments

2.1. Materials

Reagents used in this study use medicine or cosmetics grade. To make LC, emulsifier used SCD-PEG-15S and lyso-lecithin (LyL; Maruzen, Japan). It used Bis-(N-hydroxyl ethyl, N-cetyl)malonamide (HEC-MA; Quest, France), hydrogenated dimmer acid esters (HDAE; Nippon fine chemical, Japan) and dipalmitoyl hydroxy proline (DPHP; Seppic, France). Ingredients in water phase are glycerin (LG Chemical, Korea), butylene glycol (BG; Dow Chem. USA) and betain (Ajinomoto, Japan). Also, emollients used squalane (Sophim, France) octyl dodecanol (OD; Kokyu alcohol, Japan), cyclomethicone (CM; Dow corning, USA), hydrogenated dimer acid esters (HDAE; Nippon Fine Chemical, Japan). There were used carbomer (Noveon) and behenyl alcohol (BA; Cognis, Germany) as thickners.

2.2. Devices

To make LC that used T. K Robomics (Tokushu Kika Kogyo, Japan) as an emulsification, and it used optical microscope to observe structure of particle in

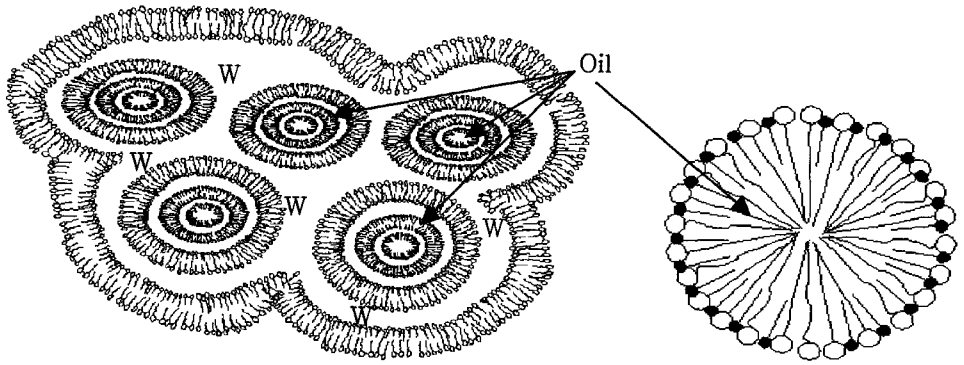

Figure 3. Schematic diagram of liquid crystalline (a) with GS and micelle (b) with polysorbate-60.

generally O/W emulsification particle. This observed and magnifies microscope by 400 to 1,600 magnifications to examine closely ternary liquid crystalline and check using polarized microscope to measure change of liquid crystalline formation. Also, it used Brookfield (Brooks, USA) to observe stability by passage time about LC.

2.3. Manufacture Method of LC

It showed method that makes LC to Figure 1. Manufacturing method makes LC, which is as following. After, measure exactly (A) phase (water-phase) of Table 1 so that total amount becomes 100 g, 75~80℃ heating until melt perfectly and keeps separately. Also, (B) measuring exactly phase (oil phase) 75~80℃ after, they melt perfectly heating separately kept. They disperse this adequately projecting (B) phase slowly to (A) phase. This time, mix the first for 3 min by 3,000 rpm that is the suitable speed. This completed emulsification reaction dispersing the second for 3 min by 3,000 rpm cooling this to 50℃. It made cooling 30℃ after made stable LC through cooling and making a vacuum process and put (C) phase of admixture in 45 ℃. This sample was precocious in 25℃ for about 72 h when perfect liquid crystalline is formed.

2.4. Moisturizing Effect

Device applied in skin moisturizing effect measurement about LC using Corneometer CM-825 and Skincon-200EX. Clinical test about skin moisturizing effect experimented according to measuring method that use at cosmetics expert and university hospital dermatology. Clinical test did to women of 20~40 years old, and tested regardless of skin type. Method of examination chose fixed branch office of both forearms. Moisturizing effect did comparison LC cream with general O/W emulsion cream (control) and measured by *in-vivo*. Test condition did temperature and humidity within fixed steady temperature and humidity room. Suitable temperature is 25℃, humidity measured under uniformity condition of 60%. Moisturizing effect test for skin measured durability because 30 min test to interval 1 h, 2 h, 4 h after using samples. Effectiveness verification about moisturizing effect of skin verified statistical significant difference to use ANOBA t-test.

3. Result and Discussion

3.1. Structure of LC

It is LC using GS, which differs structurally with basic emulsion. Usually, there are formed micelles in case of make emulsion using normally emulsifiers. If there is having two alkyl chains to hydrophilic group, dispersing GS are combined in water, bi-layer is formed. Figure 3 showed various kinds raw materials to form GS and liquid crystalline. As see in picture, it has composed by only effective raw materials forming liquid crystal. They form multi-lamellar structure selectively in case of use these raw materials. As see in Figure 3(a), whereas have micelle structures generally in O/W emulsion, Figure 3(b) showed structure of liquid crystalline although they are same things but the formation structure differs between micelles and liquid crystalline. Disperse phases of LC make to form oil droplet, and they were formed by microscopic multi-lamellar structure because GSs have a characteristic getting hydro and hydrophobic properties that is situ-

Table 1. The Optimum Composition of LC

Classification	INCI name	LC (wt%)	Control (wt%)
Water phase	Lysolecithin	1~3.00	1~3.00
	Butylene glycol	2~5.00	2~5.00
	Glycerin	1~5.00	1~5.00
	Methylparaben	0.1~0.2	0.1~0.2
	Carboxyl vinyl polymer[1)]	3~10.00	3~10.00
	Triethanolamine	0.03~0.10	0.03~0.10
	Water	to 100.00	to 100.00
Oil phase	Sodium Dicocoylethylenediamine PEG-15 sulfate	1~5.00	-
	Polysorbate-60	-	1~5.00
	Behenyl alcohol	0.1~0.2	0.1~0.2
	Squalane	3~5.00	3~5.00
	Cyclomethicone	4~6.00	4~6.00
	Octyldodecanol	4~6.00	4~6.00
	Propylparaben	0.1~0.20	0.1~0.20
	Bis-(N-hydroxyl ethyl, N-cetyl) malonamide	1~3.00	1~3.00
	Hydrogenated dimer acid esters	2~8.00	2~8.00
	Dipalmitoylhydroxyproline	0.5~0.4	0.5~0.4
Additives	Betain	0.5~3.00	0.5~3.00
	Water	1~5.00	1~5.00
Total		100.00	100.00

1) *Carbomer 940 1% solution with water*

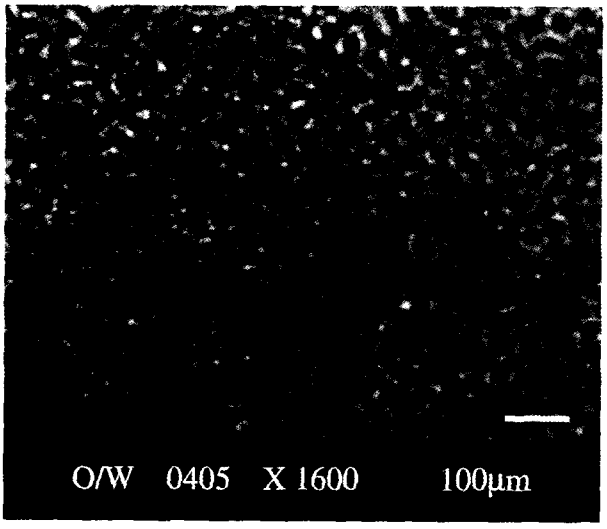

Figure 4. Picture of normal emulsion with polysorbate-60; 400 magnifications; particle size (0.42~8.62 μm)

ated on around of small droplet. Betain existed by stable state because is encapsulated on droplet inside of this liquid crystalline or loading it in hydrophilic group of multi-layer. It is expected that has an advantage storing for a long-term and interacts by delivery system acting slowly in skin.

3.2. Formation and Observation of LC

Table 1 showed formulation that can make optimum LC. It observed formation availability of this liquid crystalline using polarization microscope. These ingredients help in formation of liquid crystalline chose by raw materials and skin texture is ingredients to make by excellent quality having skin protecting function. It was stable in pH 4.0 to 10.5, and in pH 6.5 was best. The most stable viscosity value was 8,000±500 cP. Particle shapes and structures of LC were observed. Figure 4 is the microphotograph that magnify by 400 magnifications. It makes general O/W emulsion cream with polysorbate 60 as an emulsifier. As see in the picture (Figure 4), particle size was 0.42~8.62 μm (average 1.23 μm).

In case of observe by polarization, O/W emulsion's cream confirmed that liquid crystalline is not formed. Also, Figure 5(a)~(c) is the picture which checking expanding by 400, 600, 1,000 magnifications. It confirmed that very small liquid crystalline droplets are forming much. Particle size was 2~24.6 μm, and average

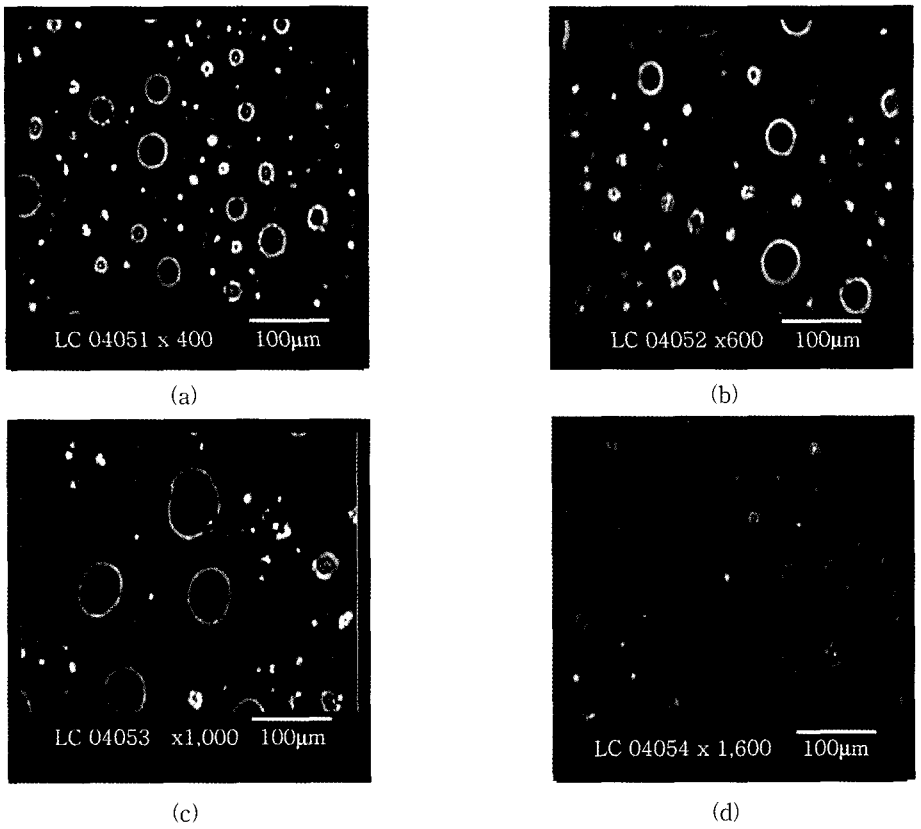

Figure 5. Pictures of liquid crystalline with Gemini surfactant by measuring polarized microscope; (a); 400 mag., (b); 600 mag., (c); 1,000 mag., (d); 1,600 mag.

particle size was 14.42 μm. Figure 5(d) is the polarization microscope that film expanding by 1,600 magnifications to examine surrounding formation structure of liquid crystalline. As see in pictures, they could confirm that forms the droplet of surrounding formation as multi-layers of liquid crystalline. Formation of LC is forecasted that two alkyl chains happen by structural characteristic of GS molecular that is linked straight to hydrophilic group. Also, this could make multi-layer with GS, LyL, HEC-MA, HDAE, DPHP, and predicted that appears by wetting phenomenon by hydrogen bond of glycerin, BG, betain in it.

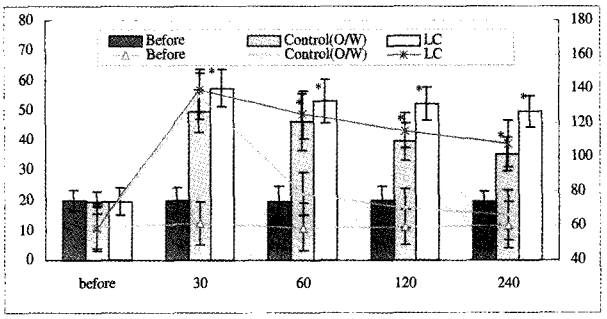

Figure 6. Moisturizing activity of the on LC compared with control O/W emulsion cream by Corneometer CM-825 and Skincon-200EX (n=10, *p<0.05).

3.3. Particle Size of LC

Particle size of LC obtained good result that measures measurement of particle size each 3 times and applied particle's distribution using particle sizer. It fills water to become 30 mL measuring exactly 5 g LC, and it measured particle size after mix to be scattered well as particle does not break by 200 rpm for 2 min. Particle size distribution formed in 19.5 μm range from 1.0 μm, and could know that average particle size is 9.87 μm in range 50% extent. Therefore, particle size that liquid crystalline appears best was about 4.0~15.5 μm. Particle size can differ gradually in case of compare particle analyzer with microscope. But, in this paper, it could get same result.

3.4. Moisturizing Effect of LC

It measured moisture effect to use Corneometer CM825 and Skincon-200EX. Clinical trial chose Korean's women 10 volunteers (20~40 age). First, it measured skin state (before) ago an experiment. It compared LC's moisture effect with general cream. Figure 6 showed result that measure moisture to use Skincon-200EX and Corneometer CM825. Incase of Corneometer CM825, moisture was 19.5±3.62 to 19.3±4.58 before treatment sample whereas moisture of after 30 min was 49.59± 6.43 in O/W emulsion (control). LC was equal level to control by 57.4±7.21 (increased 13.6%). The moisturizing effect of after 1 h was 46.15±9.41 in O/W emulsion (control). LC was equal level to control by 52.8± 7.42 (increased 12.6%). But, the moisturizing effect of after 4 h in case of O/W emulsion cream was 35.4± 5.62. LC was increased moisturizing effect by 28.3% (49.4±5.21). Therefore, it fell rapidly than LC from 1 h after stick sample in O/W emulsion cream. The reason is dehydrated fast after general O/W emulsion cream is assimilated in skin and because water preservation does not become. In case of LC is judged that water preservation is kept and displays skin moisturizing effect long hours after skin application. Therefore, it is expected that it is thing by LC making from liquid crystalline using GS. This result according to result that verify statistical significant difference using ANOBA t-test, p-value proved that keep in mind in 95% extent (p-value<0.05) when compare before treatment. When differed measurement device conclusively, moisturizing effect is difference of numerical effect, but the tendency showed that is same, it could know that sample that make from liquid crystalline is superior in moisturizing effect than general O/W emulsion cream.

4. Conclusion

This article is research of formation of liquid crystalline-lamellar gel network system, and the results were as follows.

1) Gemini surfactant applies 3.0% SCD-PEG-15S and made liquid crystalline. Besides, ingredients are helping in liquid crystalline formation were 2.0% LyL, 1.0% HEC-MA, 4.0% HDAE and 1.0% DPHP.

2) As the results of physical property of LC were as follows. The pH ranges were stable in 4.0 to 10.5, and optimum pH was 6.5. The most stable viscosity showed by 8,000±500 cP.

3) Formation of liquid crystalline observes by 400 magnifications through polarization microscope, 600 magnifications, 1,000~1,600 magnification and it examined closely liquid crystalline. As the results, analyzed structure of liquid crystalline through the polarized microscopy, it was formed around oil droplet. Sizes of liquid crystalline have 4.0 to 15.5 μm, and average diameter was 9.87 μm.

4) Moisturizing effect increased 13.6% (*P<0.05) than O/W emulsion cream (control) after 30 min of LC using Corneometer CM-825. By the way, moisture increased 28.3% (*P<0.05) than control after 4 h. There is numerical difference in result measuring by Skincone-200EX but same aspect was seen.

The reason is forecasted that it is that liquid crystalline is absorbing much water content and oil forming lamellar structure. Also, this can utilize by DDS technology of skin. Forward, this LC technology is expected that application is possible in medicine, manufacturing drug and cosmetics.

Acknowledgment

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References

1. O. B. Andre, M. Paye, and I. H. Maibach, Handbook of cosmetic science and technology, 419, Marcel Dekker, Inc., New York · Basel (2001).
2. O. B. Andre, M. Paye, and I. H. Maibach, Handbook of Cosmetic Science and Technology, 171, Marcel Dekker, Inc, Newyork (2000).
3. S. Fukushima, M. Yamaguch, and F. Harusawa, Effect of cetosteary alcohol on stabilization of oil-in-water emulsion, *J. Colloid and Interface Science*, **59**, 159 (1997).
4. T. Suzuki, M. Nakamura, H. Sumida, and A. Shigeta, Secondary droplet emulsion-Contribution of liquid crystal formation to physicochemical properties and skin moisturizing effect of cosmetic emulsion, *JSCC*, **43**, 21 (1992).
5. I. G. Lyle, U.S Patent, 5,814,323 (1998).

6. Y. Mitsuno, K. Nomaguchi, and T. Suzuki, U.S Patent, 4,767,625 (1998).
7. N. Nakanishi, Y. Matsuzawa, and N. Mikami, Moisturizing effect of amino acids and their derivatives, *Frangrance J.*, **23**, 71 (1995).
8. I. Sasaki, K. Arahane, and T. Suzuki, Application of phospholipids as recent humectant formulations, *Frangrance J.*, **23**, 56 (1995).
9. H. Kunieda, M. Tanimoto, K. Shigeta, and C. Rodriguez, *J. Oleo Sci.*, **50**, 633 (2001).
10. D. Imbert and R. Randall, Topical delivery with liposomes, *Cosmetics and Toiletries*, **110**, 32 (1995).
11. I. Y. Kim, C. K. Zhoh, and H. C. Ryoo, Formation of Proitamin-B5 liquid crystal with hydrogenated lecithin and Its effectiveness of moisturizing activity, *J. of Korean Oil Chemists' Soc.*, **19**, 10 (2002).
12. I. Y. Kim, G. B. Lee, C. K. Zhoh, and S. W. Kang, Formation of lipid-LCG with hydrogenated lecithin, *J. of Korean Oil Chemists' Soc.*, **19**, 10 (2002).
13. W. Schuberth and J. F. Hanny, U.S Patent, 4,301,023 (1981).
14. M. Yamashita and K. Kameyama, Scanning electron microscopic study of microstructure of O/W emulsion, *3rd ASCS*, 287 (1997).
15. J. Andrew Bevacwua, M. Konstantinos Lahanas, and G. Cioca, Liquid crystals in multiple emulsions, *Cosmetics & Toiletries*, **106**, 53 (1991).
16. H. E. Junginger, Colloidal structures of O/W creams, *Pharmaceutisch Weekbad Scientific Edition*, **6**, 141 (1984).