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Liquid crystal make-up remover: Conditions of formation and its cleansing mechanisms

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Synopsis

Oily residues of make-up cosmetics tend to remain in the sulcus cutis and pores of the skin. In order to remove them without causing skin irritation, two particular properties are required: 1) immediate dissolution and/or dispersion of remaining cosmetics with a make-up remover, and 2) the facility of rinsing off the remover containing the residual cosmetics from skin. In order to meet the former need, the remover must be lipophilic, and for the latter, it must be hydrophilic. Therefore, two opposite properties are required in one product. We have been able to overcome this problem by using a lyotropic liquid crystal system.

A liquid crystal that consists of a branched alkyl surfactant and a polyol is able to contain a large amount of oil. As it is bicontinuous to both oil and water phases, the oil-based cosmetics can be dissolved and dispersed easily by rubbing skin with the remover. During the rubbing process, a phase transition occurs, thus enhancing the dissolution of the oily impurities due to the disruption of the liquid crystal structure. In the rinsing process, the oil phase that dissolves the oily residues can be removed from the skin by self-emulsification. The sequential cleansing mechanism of rinsing process is 1) reformation, by addition of water, of a lamellar liquid crystal (LC) containing the oily residues, 2) phase transitions: LC → O/LC → O/W emulsion, and 3) removal of the emulsion. During these processes, the interfacial tension between oil and water phases becomes very low and forms fine emulsion droplets, which means they can be rinsed off very easily with the dispersion force of Brownian movement.

INTRODUCTION

Remaining cosmetics, having finished their use at the end of the day, plus accumulated sebum, are considered to be useless dirt. Oily cosmetics such as waterproof foundations, well protected from sweating, eyeshadows, and lipsticks are especially difficult to sufficiently cleanse by surfactant types of cleansers and soaps. It is usually considered that solvent-type cleansers such as cleansing creams or cleansing oils are useful for removing the cosmetic residues. However, they tend to remain on the skin because they have not been developed for better removal from the skin after they disperse or dissolve cosmetics. Usually they are wiped off with a tissue; however, this method may result in skin damage by the scrubbing motions and in incomplete removal of cosmetics from the skin.

Under these circumstances, it is necessary and critical for the cleansers to be rinsable, as well as being able to dissolve and disperse cosmetics efficiently to protect the skin from physical damage. In order to dissolve the oily cosmetics, the cleanser must be lipophilic, which means that it should be an oily type or possess low interfacial tension to the oil (1). On the other hand, in order to be rinsable, it must be hydrophilic. Therefore, to meet both needs, the ideal cleanser must satisfy these two opposite features at the same time. We found that a liquid crystal system consisting of nonionic surfactants and polyhydric alcohols can contain a large amount of oil; thus it can cleanse oily dirt well. Moreover, it can be rinsed off very easily by simply washing with water. In this report we discuss conditions of the formation of the liquid crystal, the cleansing mechanism, and the advantages as a make-up remover.

EXPERIMENTAL

MATERIALS

All surfactants used were commercially available. Polyoxyethylene(20) octyldodecyl ether (EOD-20) was used as a nonionic surfactant for the remover. For comparison, variable numbers of ethylene oxides attached to polyoxyethylene octyldodecyl ethers (EOD-n), polyoxyethylene(20)oleyl ether (EO-20), polyoxyethylene(20) sorbitan monostearate (ESMS-20), polyoxyethylene(60)sorbitol tetraoleate (ESTO-60), polyoxyethylene(15)glycerol monostearate (EGMS-15), and polyoxyethylene(60)hydrogenated castor oil (EHCO-60) were used (Kao Co.).

Tris-(2-ethylhexyl)-glyceride (Kao Co., Excepal TGO) was used as the oil component of the liquid crystal remover. The oil-soluble 2-ethylhexyl-p-methoxycinnamate (Givaudan Co., Parsol MCX), which possesses the maximum absorbance at 290 nm, was used as the marker for the analysis of oily residue. The glycerol used was reagent grade (Wako Chemical Industry Ltd.). Water was deionized and distilled. Materials used for the model oily residue were ceresin (Nikko Rika Co.), microcrystalline wax (Witco Chemical Co.), carnauba wax (Noda Wax), and diisostearyl malate (Nisshin Co.,), and were of cosmetic grade. D. & C. Red No. 7 and titanium dioxide (Miyoshikasei Co.) of cosmetic grade were used as pigments.

METHODS

Conditions of skin surface. Conditions of the skin surface were observed and photographed with a direct skin analyzer (DSA) (2), which is a photo-magnifying scope attached to a TV camera and a fiber light unit developed by cooperation of Kao Co. and Scalar Co., with 50× to 200× magnification of skin images. Morphological study of skin was also made by microscopic obesrvation of skin replicas.

Physiological effects of cleansing methods. Two kinds of cleansing methods were carried out once a day throughout the three-week testing period. One was rinsing off with water and the other was wiping off the remover with tissue after applying either O/W cleansing cream or liquid crystal gel (0.075 mg/5.0 cm^2) on the upper arms and massaging for 25 seconds. Observations and image analysis of corneocytes isolated from stratum corneum by the tape stripping method were made twice, before and after the three-week treatment, by using a scanning image analyzer (JEOL Co. Model SIA-3) attached to a color video microscope system (×1000) (Wilson Co. Model CVM7000). The sizes of corneocytes were analyzed by using an image analysis computer program (PIAS Co. LA-500). The corneocytes from nine panelists were examined and average sizes of 40 to 50 cells were calculated for each test.

Amount of remaining remover. The mixture of a nonionic surfactant (EOD-20), TGO, Parsol MCX, and 70 wt% aqueous solution of glycerol in the ratio of 25:48:2:25 by weight, as a model formula of make-up remover, was applied to the forearm (350 mg/32 cm^2). After rubbing for 25 seconds, the mixture was rinsed off with water. The remaining remover was extracted by wiping three times with cotton soaked with a mixture of acetone and ether (1:1). Quantitative analysis of Parsol MCX as the marker was followed by using an ultraviolet visible spectrophotometer (λ = 309.2 nm) (Beckman Co. Model DU-7) after it was extracted from the cotton with 20 ml of $CHCL_3$ and CH_3OH (3:1).

Cleansing ability. A mixture of 5 wt% of ceresin, 5 wt% of microcrystalline wax, 10 wt% of carnauba wax, 70 wt% of diisostearyl malate, 8 wt% of D. & C. Red No. 7, and 2 wt% of titanium dioxide was used as a model of oily cosmetics. It was applied to the forearms (20 mg/16 cm^2). 400 mg of remover was applied, followed by rubbing for 25 seconds and rinsing with water. The cosmetic residue was observed with a DSA, and its amount was converted into numerical values with an image analyzer in order to compare the cleansing ability. In this study, the amount of residues accumulated in the pores and sulcus cutis of the skin was neglected, and only the surface residue was taken into account.

Phase diagrams. The samples used for phase equilibria were weighed directly into glass test tubes with teflon-sealed screw caps and were kept in a thermostated bath at various temperatures. Samples with high viscosity were agitated at a high temperature in order to accelerate the achievement of equilibrium. The different phases were identified by visual observation with and without crossed polarizers. The liquid crystalline phase structure was identified by its optical texture (3,4) by means of microscopic observation with polarized light, and by X-ray diffraction (5,6). A Nikkon XF-2 microscope equipped with thermoregulator (Mettler Co., Thermosystem FP-800), a small-angle X-ray diffractometer (Rigaku Co., Geigerflex RAD-rB equipped with small-angle X-ray diffraction camera), and a wide-angle diffractometer (Shimadzu Co., XD-7A) were used to examine and confirm the structure and the state of the liquid crystalline phase. Cu-Kα radiation (λ = 1.54 A) was used in both X-ray diffractometries.

Rheological properties. The rheological properties of emulsions were measured with a coaxial-cylinder viscometer (Rotovisco RV-2 of Haake Co., LTD.).

Droplet size distribution of emulsion. The droplet size distributions of emulsions were determined with a Coulter Counter (Model TA-II) and a Coulter Submicron Analyzer (Model N4).

RESULTS AND DISCUSSION

STATE OF REMAINING MAKE-UP COSMETICS AND PROBLEMS WITH CONVENTIONAL MAKE-UP REMOVER

Oil-based cosmetic residues, such as waterproof foundations and eyeshadows, often remain on the skin even after cleansing with a make-up remover. By using a direct skin analyzer, the skin surface was observed with 200× magnification value, and the oily impurities were found to remain within the pores and sulcus cutis of the skin even though the crista cutis of the skin seemed to be clean (Figure 1). A similar tendency was observed with any kind of cleansing product.

In general, make-up removers are of a solvent type. The principle of cleansing with a solvent-type remover is dissolving and dispersing oily impurities into the oil base. They are directly applied to the skin, followed by dissolving the impurities by rubbing, and then removed. The schematic illustrations in Figure 2 show the cleansing process of two kinds of cleansing creams, water-in-oil (W/O) and oil-in-water (O/W) types, which are both typical solvent-type make-up removers. Their fundamental cleansing mechanisms are the same in terms of dissolving and dispersing oily impurities within the oily phase of the emulsion, but the consecutive removal process is different. A W/O cleansing cream can easily dissolve oily impurities due to its oil-based outer continuous phase, though it is incapable of being rinsed off, and is usually wiped off. An O/W cleansing cream, on the other hand, cannot dissolve oily impurities immediately after the application because of its water-based continuous phase. The rubbing, however, induces evaporation of water and coalescence of oil droplets in the emulsion, which leads to phase inversion from O/W to W/O. Then the oil-based impurities are dissolved in it. Since a W/O emulsion formed by phase inversion still contains hydrophilic emulsifier that can produce an O/W emulsion, the cleansing cream can disperse in water by reinversion during the rinsing process. An O/W cleansing cream, therefore, can be removed by either the wipe-off or rinse-off method, but the efficiency of the latter has not yet been seriously considered.

The physical manipulation of wiping off greatly contributes to the cleansing ability of the conventional make-up removers. Its physiological influences on human skin, how-

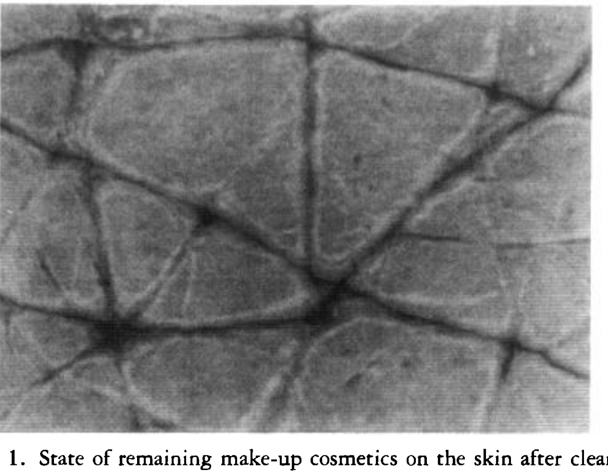


Figure 1. State of remaining make-up cosmetics on the skin after cleansing.

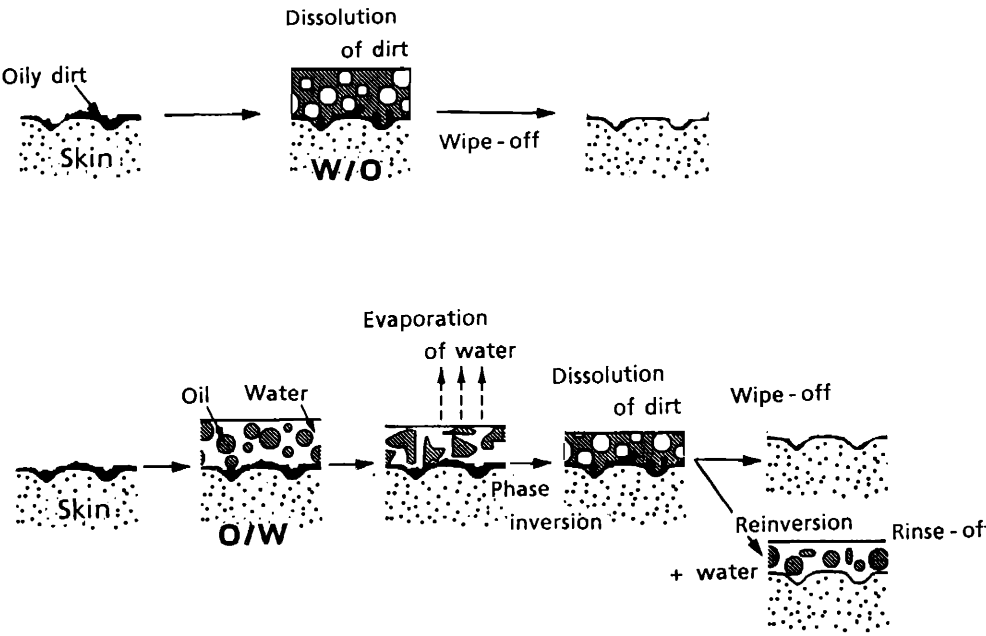


Figure 2. Schematic illustrations showing cleansing processes of two types of cleansing cream.

ever, were speculated as a cause of skin irritation and skin trouble by the physical trauma of wiping off. The physiological influence in terms of change in the area size of corneocytes on human upper arms was studied after treatment with two different kinds of cleansing methods: wiping off with tissue and rinsing off with water. Figure 3 shows the comparison in area size of corneocytes isolated from the surface of stratum corneum after three weeks of treatment. The size of corneocytes isolated from the wiped-off area became smaller than those of the rinsed-off and control areas. Within the two products of O/W cleansing cream (rinsing-off type) and liquid cystal gel, the difference was not significant. It appears that only the physical means of the removal process of cleansing products contributes to the size of corneocytes. We suspect that the wiping, a physical stress, stimulated the skin turnover, thus bringing immature corneocytes to the surface of the stratum corneum. Furthermore, the texture of the skin surface with rinsing-off treatment obviously looked better compared to that observed after wiping-off treatment (Figure 4).

CONCEPT OF A NEW MAKE-UP REMOVER AND REQUIREMENTS OF FORMATION OF LIQUID CRYSTAL MAKE-UP REMOVER

Several features and characteristics are required for an ideal make-up remover that can remove oily materials effectively without damaging the skin. Here four characteristics and formulating technology required in such a product are shown:

1) Easy to apply to the skin. → Structural system retaining a large amount of oil.
2) Dissolves oily dirt quickly. → Oily system or a system of low interfacial tension to oil.
3) Easy to rub. → Thixotropic property.
4) Easy to rinse off. → Hydrophilic or self-emulsification property.

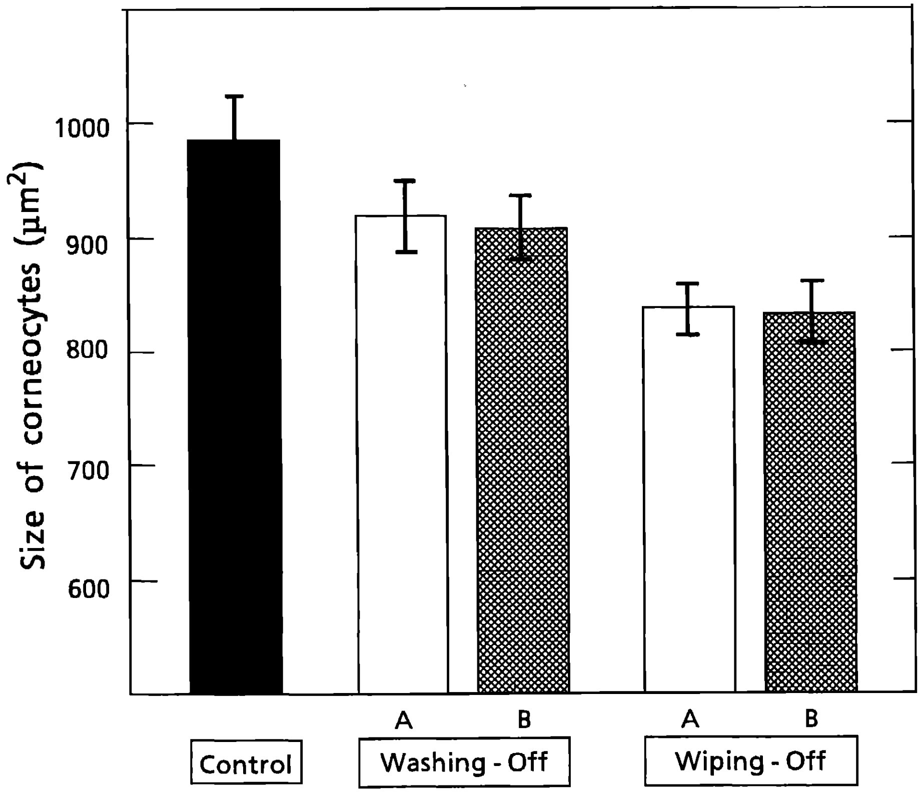


Figure 3. Area sizes of corneocytes isolated from the surface of the human stratum corneum where the different cleansing methods were undertaken for three weeks. A: a cleansing gel. B: a cleansing cream. Control: non-treated skin.

In order to satisfy the antagonistic conditions of 2) and 4), possessing oily and hydrophilic properties simultaneously, a bicontinuous liquid crystalline system composed of oil, water, and surfactant was chosen. A liquid crystal made of higher associates of amphiphilic molecules and a lamellar liquid crystal can retain oil and water in the lipophilic and hydrophilic moieties, respectively. It is known that fine emulsions can be formed when liquid crystals are formed as an intermediate stage of the emulsification process (8–11). Using these properties, the oil phase dissolving the dirt can be easily dispersed in water as fine droplets.

In such a case, it is important to choose a surfactant that yields a liquid crystalline structure easily and does not remain on the skin. In general, surfactants with branched alkyl chains effectively form higher associates such as liquid crystals, compared to surfactants with linear alkyl chains (12). The amount of removers remaining on the skin after the rinsing process was measured spectrophotometically by using Parsol MCX as a marker. The samples were prepared by mixing various kinds of surfactants and oils. Figure 5a shows the results as a function of the hydrophilic-lipophilic balance (HLB) number of the surfactant. It was suggested that a polyoxyethylene alkyl ether, which possessed branched Y-shaped alkyl chains, was suitable for this purpose.

The hydrophilic-lipophilic balance (HLB) of nonionic surfactants is due to oxyethylene (EO) chain length. The lipophilic surfactants of shorter EO chains are favorable for the

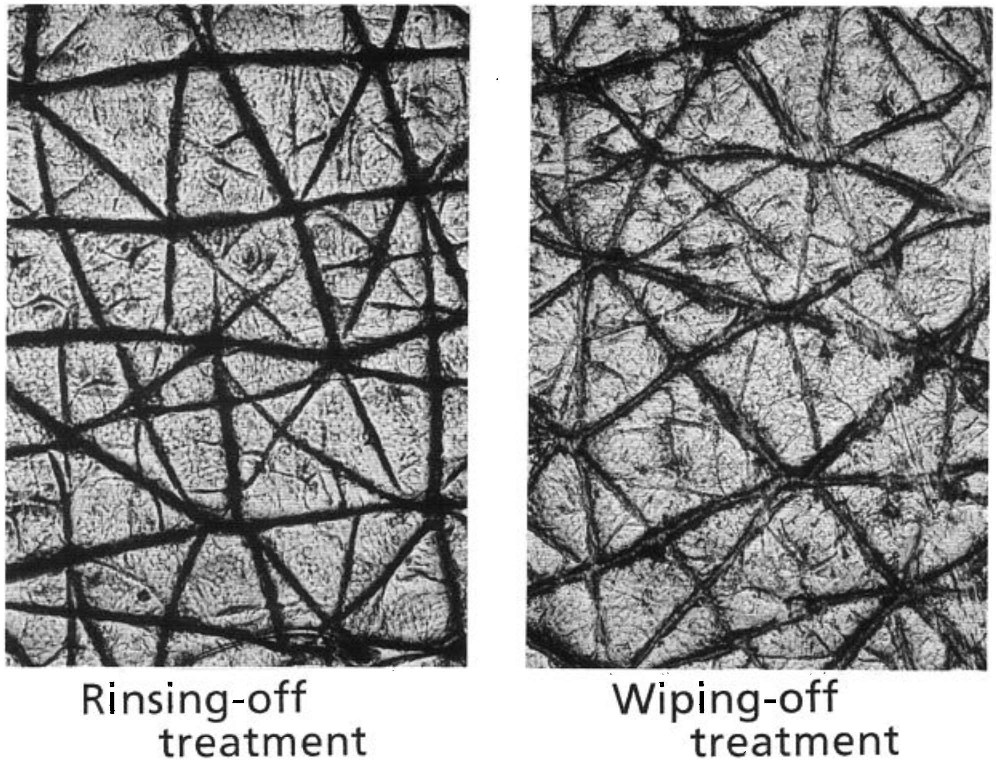
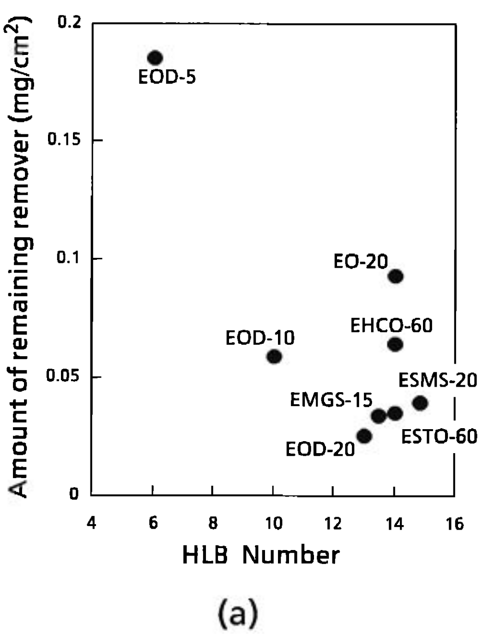


Figure 4. Skin textures of rinsing-off and wiping-off treatments.



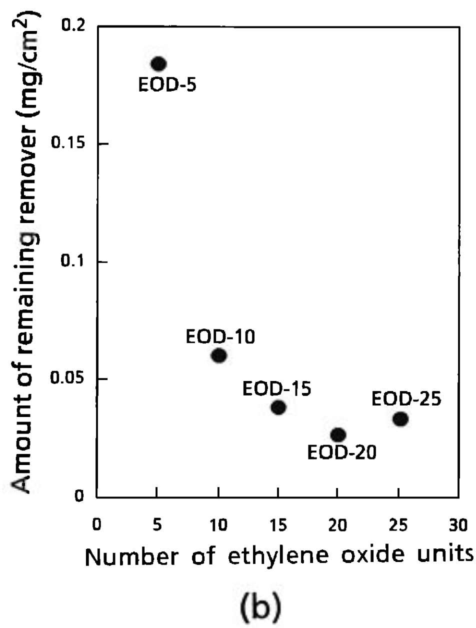


Figure 5. Amounts of remaining remover: (a) different types of surfactants; (b) various EO chain lengths.

formation of liquid crystals (13,14), whereas the hydrophilic surfactants at around 20 EO mols are more suitable for improved results in the rinsing-off process (Figure 5b).

In order to obtain the expected character, it is desirable for the surfactant to be rather lipophilic at first for the liquid crystal formation and then hydrophilic at the rinsing-off process. Therefore, a nonionic surfactant with a longer EO chain, which is better for the rinsing off, was chosen. Then the system was made lipophilic by using a polyol.

It is already known that the addition of some kinds of polyols such as glycerol and/or sorbitol depresses the cloud point (15,16), which diminishes hydrophilic property. The effect of addition of glycerol on a EOD-20/TGO/water system in a phase diagram is shown in Figure 6. Partial replacement of water by glycerol shifts the mutual solubility curve of oil and water to the left, and the one-phase solubilization area to the lower concentrations of surfactant. When the water was replaced by 70 wt% glycerol, the one-phase region projected toward the oil apex and the majority of the region became lamellar liquid crystal. This result is attributed to the effect of glycerol on the HLB of the surfactant. That is, glycerol depressed the hydrophilic property of the surfactant and

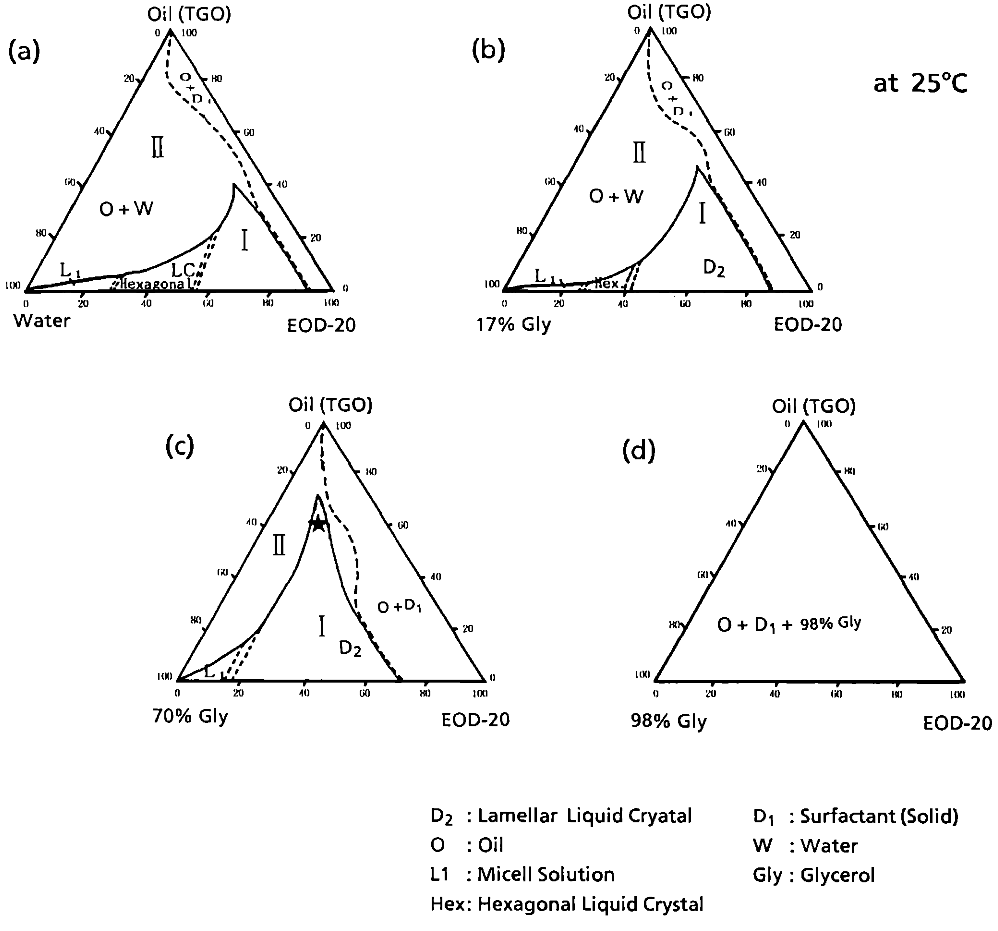


Figure 6. Phase diagrams of pseudo-three-component systems of EOD-20/TGO/water/glycerol.

Table I
Composition of Liquid Crystal Make-Up Remover

Nonionic surfactant (EOD-20)	16.0 wt%
Oil (TGO)	60.0
Glycerol	16.8
Water	7.2

promoted the formation of the lamellar liquid crystal that retains a large amount of oil. This system seems to be best balanced at 70 wt% glycerol because further addition resulted in disappearance of the one-phase region by the separation of the surfactant.

The composition of the point, which is marked with ★ in a phase diagram of Figure 6c, is presented in Table I. As shown in Figure 7, the product appearance of the composition is a transparent gel. The composition at the star showed a single peak by small-angle X-ray scattering (SAXS) measurement, while several other samples (of which the compositions are located on the extended line between the oil apex and the star) resulted in more peaks (Figure 8). The composition at the star was proved to be a lamellar liquid crystalline structure from the following facts: 1) There was a linear relationship between a series of the Bragg distances obtained from the primary peaks of the SAXS curve and C/(1-C), where C is the oil concentrations (Figure 9); and 2) there were several peaks, in the ratio of 1:1/2:1/3 . . . , in the SAXS curves of the systems containing less than 30 wt% of the oil.

Using the liquid crystalline system as a make-up remover, oily cosmetics were easily dissolved and dispersed, and the viscosity reduction that occurred during the rubbing enhanced the efficiency of dissolution. Furthermore, the system dissolving oily cosmetics was easily rinsed off with water.

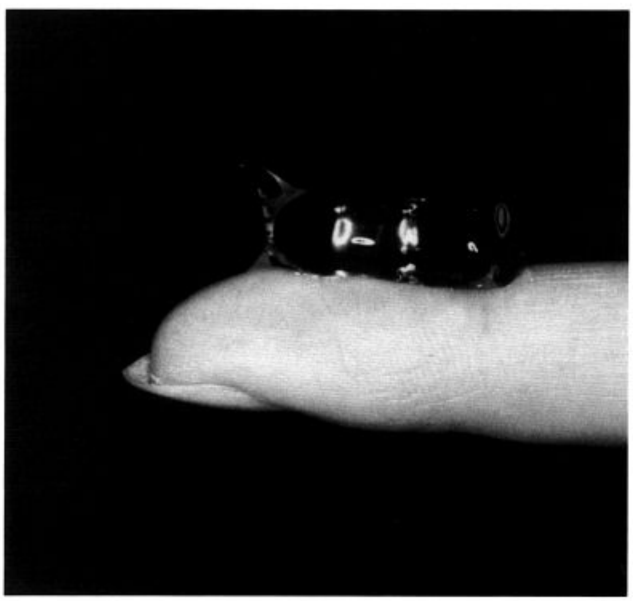


Figure 7. Appearance of liquid crystal make-up remover.

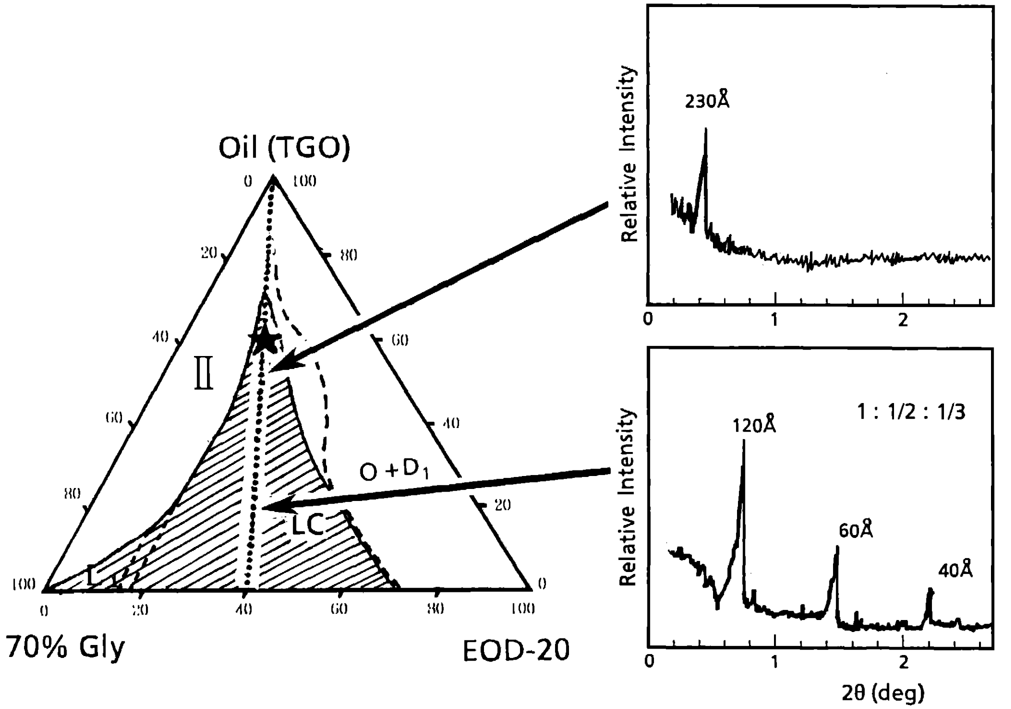


Figure 8. Patterns of small-angle X-ray scattering of gel-like phase.

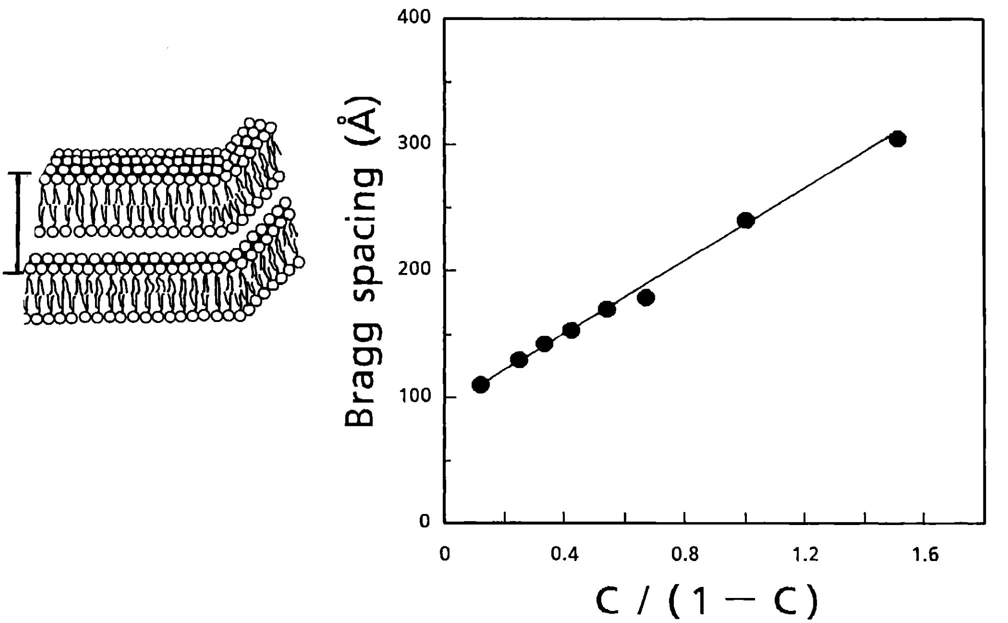


Figure 9. Changes in Bragg spacing with oil content of the gel-like phase.

CLEANSING MECHANISM AND CHARACTERISTICS OF LIQUID CRYSTAL MAKE-UP REMOVER

The cleansing ability of different surfactant systems and the droplet diameter of emulsions that formed during the rinse-off process are compared in Figure 10. The cleansing ability depended upon the droplet diameter of the emulsions, and only the liquid crystal make-up remover (LC remover), which formed a fine submicroemulsion, completely removed the model oily cosmetics. The cleansing processes of the LC remover and ordinary O/W cleansing cream are shown in Figure 11. The LC remover was applied on the marked hand. Though both make-up removers dissolved and dispersed the model oily cosmetics, only the LC remover could remove it almost completely merely by spraying with water.

The cleansing mechanism of LC remover is described in terms of phase state in a triangle phase diagram in Figure 12. In order to indicate phase transitions during the rubbing and rinsing-off processes, the water component is drawn at an apex of the diagram. The composition of LC remover presented in Table I, marked with ★ on the diagram, is identified as a lamellar liquid crystalline phase (D_2 phase) (Figure 12). In actual usage, the composition of the LC remover is supposed to shift toward the oil apex owing to the

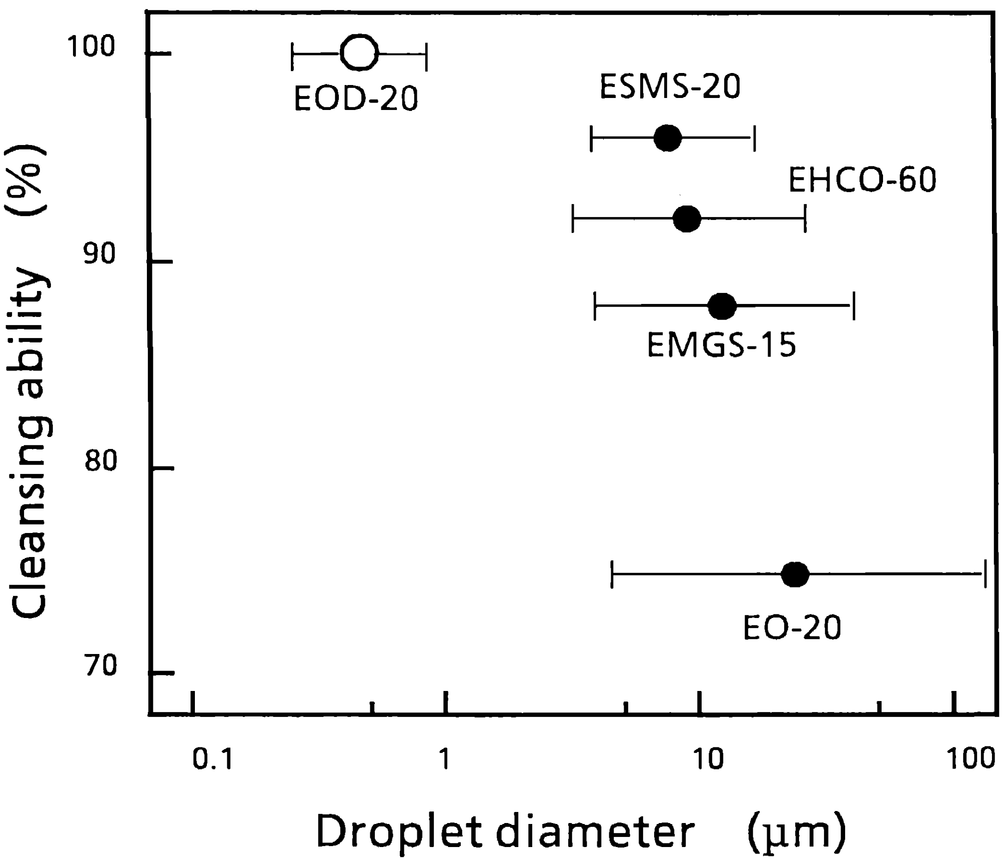


Figure 10. Cleansing ability of different surfactant systems and droplet diameters of emulsion formed during rinsing-off process.

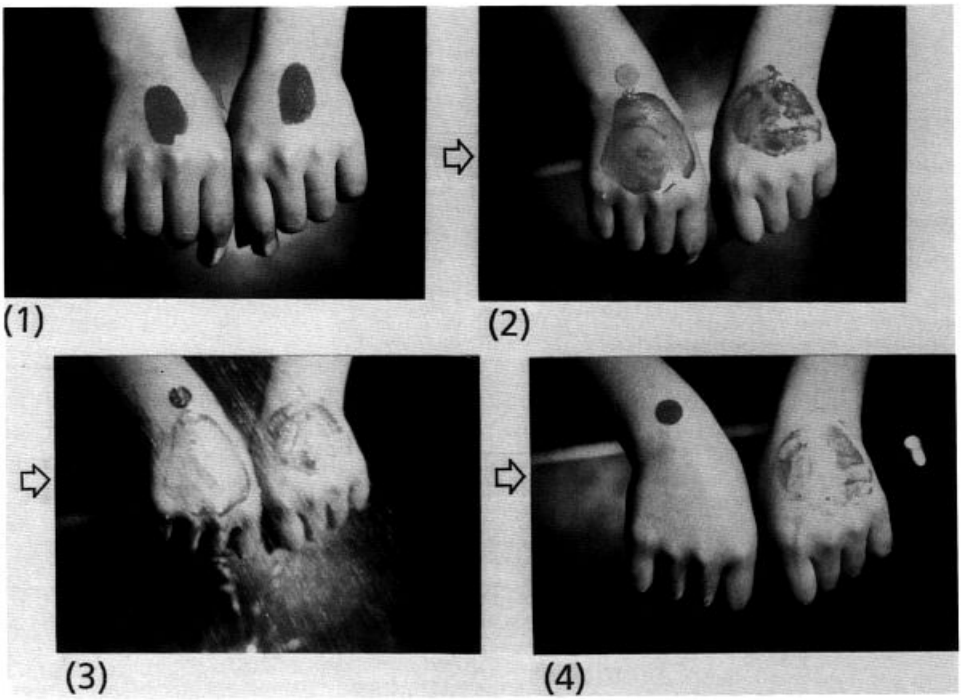


Figure 11. Cleansing process of liquid crystal remover and ordinary O/W cleansing cream.

addition of oil from cosmetics. For example, 0.1 ~ 0.4 g of foundation is generally applied for the entire face. Even if the components of the foundation are considered to be all oil, the new composition still exists in the D_2 phase when at least 1 g of LC remover is applied.

During the rubbing process, as water evaporates, the composition of LC remover shifts to the right along the dotted line. The liquid crystal dissolves oil-based dirt due to its bicontinuity (1,17). The evaporation of water abolishes the liquid crystalline structure and enhances the efficiency of dissolution by viscosity reduction. The rheological properties of the LC remover before and after the phase transition are shown in Figure 13. The LC remover itself demonstrated pseudoplastic flow with a yield value of approximately 5000 dyn/cm^2. After the phase transition, the yield value disappeared and it behaved as a low-viscosity liquid.

In the rinsing-off process, the composition shifts toward the water apex and re-enters the D_2 phase where the surfactant molecules are aligned in parallel and form an infinite aggregate. It is therefore said to be in a hydrophile-lipophile balanced state (18). The influence of glycerol, which makes the surfactant more hydrophobic, is reduced by the further addition of water, and thus the system changes to an O/W emulsion via an O/D_2 emulsion (Figure 12b). Through this process, fine emulsion droplets dissolving oil-based impurities can be easily formed because of the extremely low interfacial tension between the oil and the D_2 phase and because of the effective orientation of surfactant molecules at the oil/water interface (1,19,20). The fine emulsion droplets, which are dispersed by Brownian movement, can be easily rinsed off with water, even from the pores and sulcus cutis of the skin. On the other hand, the emulsion droplets formed

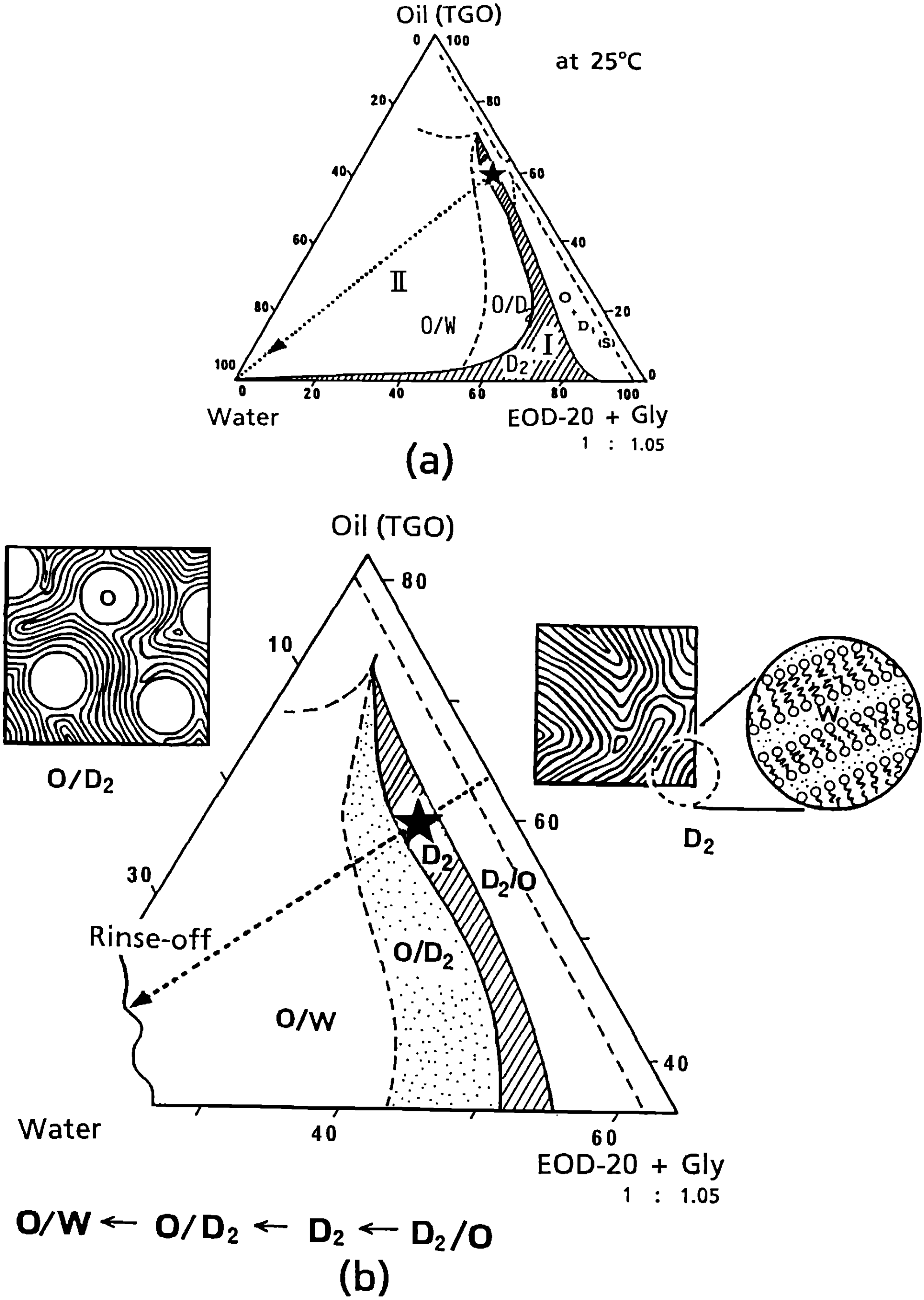


Figure 12. Changes in phase state of liquid crystal remover during rubbing and rinsing, which indicates the cleansing mechanism.

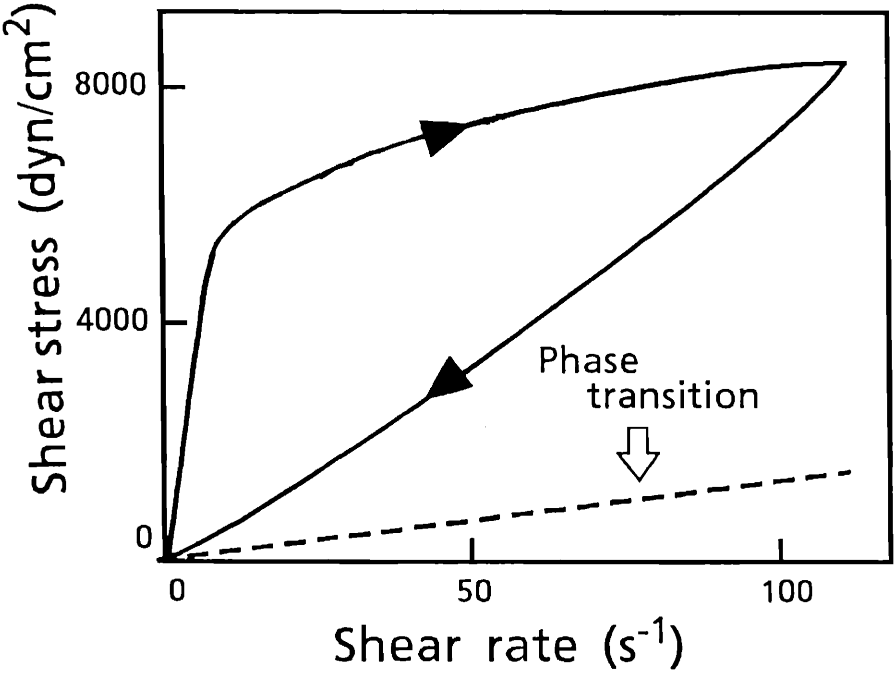


Figure 13. Rheological properties of liquid crystal remover before and after phase transition.

without passing through the D_2 phase are relatively large, and therefore are subject to coalescence and tend to re-adhere to the skin as an oil film.

Figure 14 shows the droplet diameter of emulsions formed while rinsing the LC remover, which contains different amounts of the oil component of the model impurities. The droplet diameter steeply increased when the amount of oil ratio exceeded 0.8 and as the systems became non-liquid crystal. From the above result, together with the result presented in Figure 10, a certain amount of LC remover is required for the efficient rinsing of the residues that contain the oil-based impurities. As described before, more than 1 g of LC remover results in a sufficient cleansing ability for the entire face.

Physiological studies have been done after a three-week controlled-usage test of LC remover on human upper arms (N = 9). Skin surface conditions, the area size of corneocytes, and the skin surface texture were examined. In the case of the rinsing-off method, no remarkable changes in the size of corneocytes or in skin texture were determined. It is concluded that the LC remover has a strong cleansing ability, yet is mild on the skin without causing significant damage, as is believed to be seen in the wiping-off method.

CONCLUSION

A lamellar liquid crystal containing a large amount of oil was formed by combination of a branched nonionic surfactant and a polyol. Using this liquid crystalline system as a make-up remover, oil-based cosmetics are easily dissolved and dispersed in it. Fur-

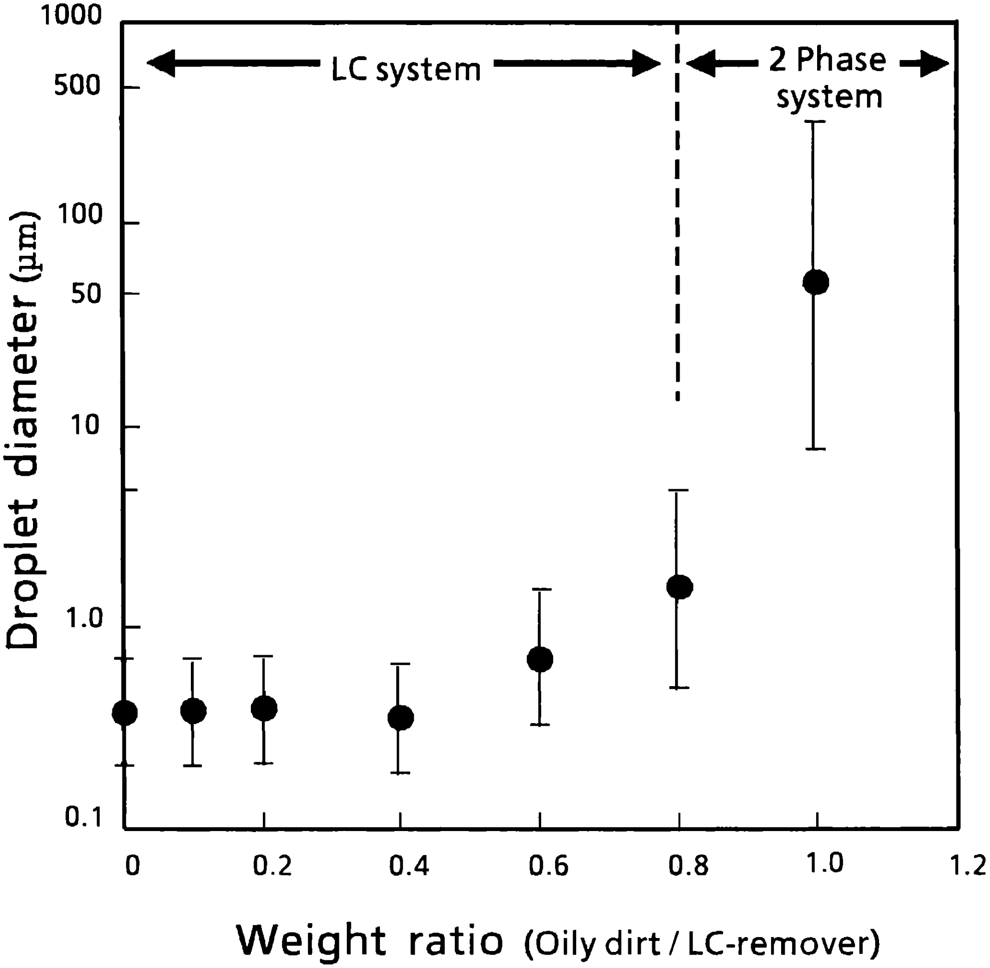


Figure 14. Droplet diameter of emulsions formed in rinsing process of liquid crystal remover with addition of various amounts of oil.

thermore, the phase transition induced by water evaporation during the rubbing enhances the efficiency of the dissolution of impurities because of the abolishment of the liquid crystal structure.

In the rinsing-off process, fine emulsion droplets are formed by passing through the liquid crystalline phase, and the oil component of the LC remover, dissolving the impurities, can be easily removed from the skin. It is concluded that the LC remover has a strong cleansing ability, yet is mild on the skin without causing significant damage.

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