報 文

Stable Emulsion Regions of Surfactant–Oil–Water and Surfactant–Oil–Water–Long Chain Alcohol Systems

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A ternary diagram for nonionic surfactant–oil–water system was studied and the region of stable and strongly opaque emulsion (the region E_1) was determined on the diagram. It was found that the E_1 region existed only within the two-phase region consisting of a viscous isotropic phase and an oil phase, and that at least 10% surfactant was necessary to obtain this region.

The quarternary system containing cetostearyl alcohol in addition to the ternary system was also examined. Addition of the alcohol produced a new stable region of strongly opaque emulsion (the region E_2) besides E_1 . The appearance of the region E_2 reduced the minimum surfactant concentration to obtain the stable and strongly opaque emulsion to about 2%. Similar effect was observed for behenyl alcohol of cosmetic grade, which is also a mixture of alcohols. However, pure alcohols of carbon numbers from 12 to 16 lacked the ability to form the E_2 region. Those of carbon numbers of 18 and 20 gave the E_2 region but only above the surfactant concentration of 5%.

1 Introduction

Emulsions, which are utilized in cosmetics and pharmaceuticals, are prepared by mixing oils and aqueous solutions usually in the presence of surfactants. Here, amphiphilic substances such as long chain alcohols, long chain acids, and monoacylglycerols are widely used to increase the stability of emulsions. Further, in order to obtain smooth and non-greasy emulsions for practical application, and to preserve them effectively from decay, it is preferable to minimize the surfactant concentration.

Several studies^{1)~7)} have already been reported concerning the formation of emulsion regions in some ternary or quarternary diagrams, and the authors also intended to examine the diagrams for a surfactant–oil–water system and surfactant–oil–water–long chain alcohol systems to add informations from the practical as well as fundamental points of view.

Lachampt *et al.*¹⁾ investigated the ternary diagrams for hydrophilic surfactant–oil–water

systems and briefly referred to the formation of a stable emulsion region. They further studied in detail the diagrams for mixed emulsifier–oil–water systems with varying ratios of hydrophilic and lipophilic surfactants, and discussed the relation between the ratio and the minimum emulsifier concentration necessary to obtain fine emulsions²⁾. However, they did not refer to further details of emulsion stability and the state of the fine emulsions.

The present study pays attention to the emulsion stability and its opacity which are the important factors for the practical emulsion products. First, the authors used a surfactant–oil–water ternary system similar to that used by Lachampt *et al.*¹⁾, and determined the region of stable and strongly opaque emulsion on the diagrams. Then, some quarternary diagrams were examined by adding long chain alcohols as the fourth component to the above three component systems.

By comparison of these ternary and quarternary diagrams, the effect of addition of long

chain alcohols on the formation of the region of stable and strongly opaque emulsions, was studied. From these results, the conditions for the formation of above mentioned regions with minimum surfactant concentrations were obtained.

2 Experimental

2.1 Materials

The surfactant used was oleyl poly (oxyethylene) (10) ether (Nikko Chemicals Co., Ltd.) which is simply called the surfactant hereafter. The cloud point of its 5% aqueous solution was 64°C. Liquid paraffin of cosmetic grade (Carnation, the product of Witco Chemical Corp.) was used which is called the oil. Water used was deionized. The long chain alcohols used were cetostearyl alcohol, behenyl alcohol, both of cosmetic grade, and five pure alcohols, the carbon numbers of which are 12, 14, 16, 18, and 20. The compositions or the purities determined by GLC and the melting points (mp) of these compounds are as follows.

Cetostearyl alcohol (Kokyu Alcohol Kogyo Co., Ltd.), C₁₆OH: 57%, C₁₈OH: 35%, C₁₄OH: 6%, others (3 peaks): 2%, mp: 54°C; behenyl alcohol (Nippon Oils & Fats Co., Ltd.), C₂₂OH: 53%, C₂₀OH: 22%, C₁₈OH: 22%, others (2 peaks): 3%, mp: 69°C; 1-dodecanol (C₁₂OH: Wako Pure Chemical Industries, Ltd.), purity 98%, mp: 24°C; 1-tetradecanol (C₁₄OH: Wako Pure Chemical Industries, Ltd.), purity: 98%, mp: 39°C; 1-hexadecanol (C₁₆OH: Tokyo Kasei Kogyo Co., Ltd.), purity: 99%, mp: 50°C; 1-octadecanol (C₁₈OH: Tokyo Kasei Kogyo Co., Ltd.), purity 98%, mp: 60°C; 1-eicosanol (C₂₀OH: Tokyo Kasei Kogyo Co., Ltd.), purity: 95%, mp: 62°C.

2.2 Preparation of Samples

A glass tube was sealed after given amounts of components were introduced, dipped in a boiling water bath for 10 min, and shaken. Further, dipping in the bath for 5 min and shaking were repeated twice. It was then cooled slowly to room temperature while being turned gently, and stored in the bath of constant temperature at 20°C.

2.3 Measurements and Terms Used

Opacity (whiteness) of samples was determined by measuring the transmittance at 550 nm using a cell of 0.15 mm thickness. Liquid paraffin

was used as a reference substance. Transmittance, T , is expressed by

$$T = I/I_0,$$

where I_0 and I are the intensities of light transmitted through the reference substance and sample, respectively.

The sample of T being less than 0.01 is defined as a strongly opaque emulsion (abbreviated as s.o.e.). The value of 0.01 was adopted referring to the opacity of most practical emulsions which show strong light scattering by dispersed droplets.

The stability of samples was determined a month after preparations. If no separation of oil or aqueous phase is observed within a month, the system is regarded as stable.

Ternary and quaternary diagrams were drawn with varying proportions of the components. The content of fourth component is indicated by its gram number per 100 g of the sum of the other three components. The identification of phases and the determination of their boundaries were made on the basis of polarizing microscopic observations, visual observations on turbidity, and transmittance measurements.

3 Results and Discussion

3.1 Surfactant-Oil-Water Ternary System

C : clear, Tl : translucent, Tb : turbid, Mw : milky white, Mw (aq) : milky white (aqueous phase separated), Os : Oil separated.

Fig.-1 General appearances of surfactant-oil-water system.

Fig.-1 shows the general appearances of the surfactant (S)-oil (O)-water (W) ternary system. C, Tl, and Tb denote the regions of clear, translucent, and turbid systems, respectively. Mw is the region of a stable milky white system which includes a "stable s.o.e. region" as shown later. Mw (aq) is the region of an unstable milky white system, where the aqueous phases are easily separated. The system in a region Os readily separated an oil phase.

Fig.-2 shows the diagram of T for the same ternary system. On either side of a relatively low water content or a relatively low oil content, T was considerably high. The change in composition of the system from the middle part to the bottom of the diagram caused the decrease in T , and the increase in opacity. The s.o.e. region was divided into two parts; a stable (E_1) and an unstable s.o.e. regions as shown in **Fig.-2**. Samples in E_1 were usually semi-solid state, whereas in the unstable s.o.e. region, samples were fluid and they readily separated aqueous phases.

Fig.-2 Transmittance of surfactant-oil-water system.

The light scattering from the emulsion droplets may be generally expected to be small and T may be high, when the droplets are too fine or too coarse compared with the wave length of the visible light. Change of the composition along the direction "a" in **Fig.-2** caused the decrease in the size and the number

of oil droplets, resulting in the increase in T . The increase in T with changing composition along the direction "b" in **Fig.-2** may be explained by the increase in the size of oil droplets and probably by the decrease in the difference of refractive indices between a dispersed phase (oil) and a continuous phase.

Fig.-3 shows the ternary phase diagram for the same system surfactant-oil-water. N and M denote neat and middle phases. I_1 , I_2 , and I_3 are different viscous isotropic phases. L_1 is the aqueous micellar phase. Oil phase region was found to be extremely narrow and limited only in the vicinity of the oil corner of the triangle. No attempt was made concerning the determination of the boundary of the oily isotropic phase region which had been presented by Lachamp *et al.*¹¹. E_1 is the same region that has been shown in **Fig.-2**.

A diagram for the same ternary system as in the present study has been presented in a schematic form by Lachamp *et al.*¹¹. They divided a micellar phase into two regions, *i.e.*, a micellar solution and an emulsoid. The authors denoted these regions as a single phase L_1 , because they seemed to differ from each other only in their appearances due to their micellar sizes.

I_1 phase, which is noted as a gel by La-

Fig.-3 Surfactant-oil-water phase diagram.

champt *et al.*¹⁾, has been considered to be a random suspension of the cylindrical micelles⁹⁾. It exhibits high elasticity and high consistency.

It is apparent from **Fig.-3** that the E_1 region is confined in the two-phase region, I_1 +oil, although Lachampt *et al.* did not refer to this region in detail. The stability of the emulsion in E_1 can be explained by the fact that the viscous isotropic phase I_1 constitutes the continuous phase. The high elasticity and high consistency of the emulsions in E_1 may be interpreted as the appearance of the intrinsic properties of the I_1 phase. The three-phase region, L_1 +oil+ I_1 , was not confirmed in the present study. The region was presumed to be very narrow. Strongly opaque O/W emulsions were formed in the two-phase region, L_1 +oil, but they easily separated aqueous phases. Hence, this region does not belong to the stable s.o.e. region.

Friberg *et al.*³⁾⁻⁶⁾ reported that a sudden increase in stability of an emulsion occurred when the composition was varied. They explained the phenomenon as that the lamellar mesomorphic phase (neat phase) became to coexist with aqueous and oil phases. In the present experiment, however, only the region of the emulsions stabilized by the presence of the I_1 phase was confirmed as a stable s.o.e. region. If the oil content was held constant and the surfactant concentration was raised from the point "c" in **Fig.-3**, also a sudden increase in stability was observed with the abrupt rise in viscosity. A sudden increase in stability occurred almost at the point "d" where the I_1 phase would begin to coexist. Thus, when the present results are compared with those of Friberg, it is evident that the mesomorphic phases differently contribute to the stabilization of emulsions. Such a difference seems to be due to the difference in the constituents adopted. Namely, Friberg used nonylphenyl poly(oxyethylene) (9) ether-*p*-xylene-water system⁵⁾. In the ternary diagram studied by Friberg, the neat phase is the most predominant phase, but the middle phase is very narrow and the I_1 phase is not seen, the latter two being more hydrophilic phases than neat phase.

Thus, it is found that the s.o.e. region is formed only within the two-phase region where

I_1 and oil phases coexist, although the emulsions in E_1 may not be called an O/W emulsion, since the continuous phase is a mesomorphic one. It is also apparent from **Fig.-3** that at least 10% surfactant is necessary to obtain the stable s.o.e. in the present ternary system.

3.2 Quarternary System Containing Cetostearyl Alcohol

Fig.-4 shows the stable and unstable s.o.e. regions when 2% cetostearyl alcohol is added. By comparing **Fig.-4** with **Fig.-2**, it is confirmed that the addition of 2% alcohol results in the shift of the whole s.o.e. regions toward the lower surfactant concentrations. The stable s.o.e. region of the quarternary system is composed of two sub-regions; one in the higher, and the other in the lower surfactant concentration regions. The former region corresponds to the E_1 region of the ternary system, but the region is slightly shifted as compared with E_1 in **Fig.-2**. The latter region is termed here " E_2 ". The emulsions in E_1 in **Fig.-4** showed highly viscous properties similar to those in E_1 in **Fig.-2**. The emulsions in E_2 were in general semi-solid, although they showed less resistance to flow than those in E_1 .

E_1, E_2 : stable s.o.e. regions.

Fig.-4 Transmittance of quarternary system containing 2% cetostearyl alcohol.

Fig.-5 and **6** show the quarternary diagrams when the cetostearyl alcohol content was varied from 0 to 4%. From these figures, the following tendencies will be confirmed.

1) The E_1 region shifts toward the lower surfactant concentration as the alcohol content increases.

2) The E_2 region begins to appear when the alcohol content reaches about 1.5% and the E_1 region almost disappears when the alcohol content increases up to 4%.

3) E_1 and E_2 regions coexist when the alcohol content is between 1.5% and 3% (the diagram of 3% alcohol is not shown).

4) On the lower oil content part of the s.o.e. region, E_1 and E_2 are separated from each other, the unstable and fluid s.o.e. region lying between them. In the higher oil content region, E_1 and E_2 become contiguous.

5) The further increase of the alcohol content shifts the E_2 region toward the lower oil content. The resultant E_2 region becomes considerably narrow.

Fig.-5 Stable s.o.e. regions in quaternary systems containing 0~1.5% cetostearyl alcohol.

Fig.-6 Stable s.o.e. regions in quaternary systems containing 0~4% cetostearyl alcohol.

The emulsions in E_2 are stabilized by the presence of the hydrophilic surfactant and cetostearyl alcohol, and they are presumed to be closely related to the emulsions studied by Barry *et al.*^{9)~13)} and Talman *et al.*^{14)~16)} in the emulsion structure. Barry referred to the self-bodying action as the interaction of a long chain alcohol with a hydrophilic surfactant solution to form a visco-elastic gel-network in the continuous phase of O/W emulsion. The E_2 region in

this study might correspond to the composition range where such an action can play a role to stabilize the emulsions.

The anisotropic structure was often observed around the oil droplets of the emulsions in E_2 . This is presumed to be a liquid crystalline structure, which might be similar to that reported by other authors^{12), 13), 18)~20)}.

Thus, by adding cetostearyl alcohol to the surfactant-oil-water ternary system, it becomes possible to reduce the minimum surfactant concentration to a great extent which is necessary to prepare a stable emulsion. In this way, if 4% alcohol is added, a stable emulsion can be obtained with least possible surfactant concentration of about 2%, over the wide range of oil content from about 10% to 70%. In fact, cetostearyl alcohol is used widely in practical O/W emulsions in conjunction with some surfactants. So, it seems likely that such a region as E_2 has been utilized in the emulsion formulations of cosmetics and pharmaceuticals. Therefore, it may be worthwhile to study the conditions to obtain a wide composition range of the region E_2 .

Fig.-7 Extension of large transmittance region with cetostearyl alcohol content (0~6%).

Fig.-7 shows the extension of the large transmittance region ($T \geq 0.5$) with the cetostearyl alcohol content (0~6%). The stable s.o.e. region of 6% alcohol content is also shown in Fig.-7. The large transmittance region

extended toward the oil corner of the diagram as the alcohol content increased. This occurred probably because micelles became more swollen with increasing amount of the alcohol to solubilize much more oil. Furthermore, if the large transmittance region extends with increasing cetostearyl alcohol content, the E_1 region is expected to shift and eventually almost disappear. As shown in Fig.-7, when the alcohol content is 6%, the stable s.o.e. region consists only of the E_2 region as a result of the entire disappearance of E_1 .

3.3 Quarternary System Containing Various Long Chain Alcohols

Fig.-8 shows the diagrams of quarternary systems in which the fourth components are cetostearyl alcohol, $C_{12}OH$, $C_{16}OH$, and $C_{20}OH$. In each diagram of Fig.-8, the oil content is kept constant at 50% and two variables are surfactant and alcohol contents. Here, the alcohol content is also shown as an additional amount (%) to the total amount (equal to 100%) of surfactant, oil, and water. Dashed curves represent the equi-transmittance curves of $T=0.01$. Areas with shadows are the stable s.o.e. regions. The upper part than the dashed curves is the region of T larger than 0.01, namely the

region of decreasing opacity. In the region lower than the solid curves, emulsion stability tended to decrease, separating aqueous phase.

3.3.1 Cetostearyl Alcohol

Fig.-8 (a) shows the diagram for the system containing cetostearyl alcohol as a fourth component. As the alcohol content increased, the E_1 region shifted toward the lower surfactant concentration and became narrow. when the alcohol content was about 3.5%, E_1 region entirely disappeared. This disappearance of E_1 may be caused by the increase in T with the increasing amount of the alcohol. For example, when the surfactant concentration was kept constant at 15% and the alcohol content was gradually increased, T reached 0.01 at the content of about 2%, and rose up to 0.5 at 3.2%. When the content was 3.2%, no oil droplets were seen under the optical microscope, and so-called microemulsion might form. In the upper part of E_1 in Fig.-8 (a), the rheological properties were similar to that of I_1 phase. At the boundary of the upper and lower parts of E_1 , viscosity changed abruptly, and in the lower part, the system remained semi-solid but turned to show less resistance to flow. So, the influence of I_1 phase may be restricted to the upper part of E_1 . In the lower part of E_1 , the continuous phase structure may be much weaker than that of I_1 phase. Below E_1 region, emulsions were fluid, and ready to separate aqueous phases.

E_2 region began to appear at the lower surfactant concentration when the alcohol content reached about 1.5%. Owing to this appearance of E_2 , the minimum surfactant concentration required for obtaining stable s.o.e. can be effectively reduced to about 2%, if more than 1.5% alcohol is added. Droplets became finer and T exceeded 0.01 above the E_2 region. T also exceeded 0.01 below the E_2 region but this is due to the oil droplets becoming larger because of insufficient surfactant concentration.

The processes of the shift and disappearance of E_1 , and the appearance of E_2 with the increasing amount of the alcohol corresponds to those shown in Fig.-5 and 6.

3.3.2 $C_{12}OH$

Fig.-8 (b) shows the diagram for the system containing $C_{12}OH$ as a fourth component. In this case, stable s.o.e. region of E_1 appeared

Fig.-8 Stable s.o.e. regions in quarternary systems (oil : 50%). Dependence upon $C_{12} \sim C_{20}$ alcohol addition.

but E_2 was lacking. Thus, $C_{12}OH$ was proved not effective as a stabilizer for the emulsion through the formation of E_2 region.

3.3.3 $C_{16}OH$

Fig.-8 (c) shows the diagram for the system containing $C_{16}OH$. Emulsions in the " E_2 " region was semi-solid but on storage they tended to separate oil phases. As a result, only the E_1 region remained as the stable s.o.e. region. In the case of the system containing $C_{14}OH$, similar results were obtained, although not illustrated here.

3.3.4 $C_{20}OH$

Fig.-8 (d) shows the diagram for the system containing $C_{20}OH$. For the system containing $C_{18}OH$, a similar diagram was obtained. $C_{18}OH$ and $C_{20}OH$ gave the E_2 region in addition to the region E_1 , but only above the surfactant concentration of about 5%. Below about 5%, emulsions had been semi-solid for a few days or a few weeks after preparation, but afterwards they turned fluid and separated aqueous phases. The separation of the emulsions was accompanied by the deposition of crystalline-like materials, probably the alcohol. The lower the surfactant concentration became, the sooner occurred these phenomena. Similar phenomena were presented by other authors^{17),20)}. Fukushima *et al.* discussed such phenomena from a view point of polymorphism of the alcohols^{17),18)}.

3.3.5 Comparison of the Alcohols

$C_{12}OH$ gave no E_2 region. $C_{14}OH$ and $C_{16}OH$ gave the E_2' region in which the emulsions were semi-solid but unstable. So, according to the concept of Barry's, the self-bodying action does not appear in the case of $C_{12}OH$, while in the case of $C_{14}OH$ and $C_{16}OH$, the action may

appear to some extent but on storage it may be weakened. $C_{18}OH$ and $C_{20}OH$ gave the E_2 region but its minimum surfactant concentration could not be reduced to less than about 5%. On the other hand, cetostearyl alcohol, whose main components were $C_{16}OH$ and $C_{18}OH$, gave E_2 region extending over a wide range of alcohol content. Its minimum surfactant concentration was about 2%, which was about 3% lower than that in the case of $C_{18}OH$ or $C_{20}OH$.

As shown in **Fig.-9**, behenyl alcohol of cosmetic grade, which is the mixture composed mainly of $C_{22}OH$, $C_{20}OH$, and $C_{18}OH$, also gave the E_2 region of sufficient stability. The minimum surfactant concentration of the E_2 region was about 2% similar to the case of cetostearyl alcohol. But the minimum alcohol content was about 2.5% which was about 1% higher than that in the case of cetostearyl alcohol. It is desirable for the practical emulsion formulations that the stable s.o.e. can be obtained in the wider composition range at the lower surfactant concentration on the diagram. From these points of view, the mixture of the alcohols such as cetostearyl and behenyl alcohols is preferable to the pure alcohols ranging from C_{12} to C_{20} , as far as the present study is concerned.

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Fig.-9 Stable s.o.e. region when fourth component is cetostearyl alcohol (CS) or behenyl alcohol (B).

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界面活性剤-油-水系及び界面活性剤-油-水-長鎖アルコール系における安定エマルジョン領域

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非イオン界面活性剤-油-水三成分系の状態図を調べ、安定かつ乳白度大なるエマルジョン領域 (E_1 領域) をその状態図上で求めた。その結果、 E_1 領域は粘ちゅう等方性相と油相からなる二相共存領域内にのみ存在すること、及びこの領域を得るためには少なくとも 10% の界面活性剤が必要であることがわかった。

次いで、この三成分にセトステアリルアルコールを加えた四成分系について調べた。セトステアリルアルコールの添加により、乳白度大なるエマルジョンの新たな安定領域 (E_2 領域) が E_1 領域のほかに生成した。この E_2 領域の出現は、安定かつ乳白度大なるエマルジョンを得るための最少界面活性剤濃度を約 2% まで減少させた。同様に混合アルコールである化粧品グレードのベヘニルアルコールについても同じような効果が見られた。しかし炭素数 12 から 16 の各アルコールは E_2 領域を生成させる能力に欠けていた。また炭素数 18 と 20 のアルコールは E_2 領域を生成させたが、いずれも界面活性剤濃度 5 % 以上の領域に限定されていた。