

A STUDY OF GEL STRUCTURE IN THE NONIONIC SURFACTANT / CETOSTEARYL ALCOHOL / WATER TERNARY SYSTEMS BY DIFFERENTIAL SCANNING CALORIMETER

Moung Seok Yoon*, Youn Bok Chung*, and Kun Han*

*Cosmetics R&D Center, LG Chemical Ltd./Research Park
#84, Jang-dong, Yusong-gu, Taejon 305-343, Korea

*College of Pharmacy, Chungbuk National University,
Cheongju, Chungbuk 361-763, Korea

ABSTRACT

Cetostearyl alcohol has been incorporated into cosmetic or pharmaceutical emulsions to give them an appropriate consistency and a long term stability. It is well known that cetostearyl alcohol forms a gel phase with a nonionic surfactant in an aqueous system, and the properties of the gel phase depend on several factors such as the ratio of fatty alcohols. The aim of the present paper is to investigate the effect of the

structural difference of the lipophilic part of surfactants on the stability of the gel phase in the nonionic surfactant / cetostearyl alcohol / water ternary systems using differential scanning calorimeter.

It is concluded that the gel phase formed by the surfactant having the bended alkyl chain is more unstable than that formed by the case of the straight alkyl chain, and we discussed the reason why the former is more unstable after long term storage by means of the measurements of the ΔH .

INTRODUCTION

O/W emulsions appear to be very complex systems and their properties can be attributed to particular structural elements, namely to crystalline and liquid crystalline gel structures. They are responsible for the consistency and the stability of emulsions.

The use of cetostearyl alcohol in cosmetic or pharmaceutical emulsions is a common practice as it forms a liquid crystal phase easily with surfactants in the emulsion systems. In this way, cetostearyl alcohol has been incorporated in formulations to give emulsions an appropriate consistency and long term stability.

Cetostearyl alcohol plays an important role in the formation of the hydrophilic gel phase in emulsions. The excess of cetostearyl alcohol that is not participated in the hydrophilic gel phase forms a lipophilic gel phase. An increase in the proportion of cetostearyl alcohol in emulsions always leads to an increased viscosity of the entire systems containing two different gel phases or one(1,2,3,4).

The structural properties of the gel phase depend on the ratio of cetyl and stearyl alcohol(5,6), the amounts and the types of surfactants(7,8,9), and the water content in these systems(2,3). It is very important to understand the structural properties of the gel phases because they directly influence the properties such as rheology and stability in o/w emulsions.

Many studies have been performed to investigate such phenomena, but there exist relatively few papers on the influence by the structural difference of the lipophilic parts of surfactants on the o/w emulsions. To survey the relationship between the expected stability of emulsions and the structural difference of lipophilic parts, we performed this study with conventional ternary systems that contain nonionic surfactants, cetostearyl alcohol (cetyl alcohol : stearyl alcohol = 6 : 4) and water using differential scanning calorimeter.

EXPERIMENTAL

Materials

The cetyl alcohol and stearyl alcohol from Yakuri Pure Chemicals Co.,Ltd. (Japan) were pure reagent grades. The cetostearyl alcohol (CSA) was a mixture of the weight ratio of cetyl alcohol : stearyl alcohol = 6 : 4 and the average molecular weight was 254.

Polyoxyethylene(15moles) oleyl ether(POE₁₅OE) and polyoxyethylene (15moles) stearyl ether (POE₁₅SE) were used as nonionic surfactants and their average molecular weight was 928 and 930 respectively. Both of them were from Nihon Emulsion Co., Ltd. and were cosmetic grades.

The deionized water was used.

Sample Preparation

For the preparation of CSA / water mixtures, the water ranged from 2 wt% to 40 wt% was heated to 70°C and added to the molten CSA at the same temperature stirring slowly with an agitator. A hydrated CSA was formed on cooling slowly below 25°C. Samples were sealed tightly and kept at 25°C for 2 weeks before the measurements were taken.

The ternary systems containing CSA, nonionic surfactants, and water were made in the range of water contents from 10 wt% to 80 wt%. The molten phase of CSA and nonionic surfactants at 70°C was added to the water phase at the same temperature and emulsified by agitating them carefully for 3min. The emulsions were cooled to 25°C and kept -15°C, 0°C, and 25°C before the measurements by DSC.

Measurements

The DSC measurements were performed with Hart Scientific differential scanning calorimeter (Model 4207) equipped with a mechanical cooling accessory. The heating and cooling cycles were carried at the rate of 1°C/min between -30°C and 80°C, and with the sensitivities of $\pm 5\mu$ cal/°C. The areas between the peak and the baseline were integrated and converted into heat amounts, ΔH .

The systems were studied through the polarized light microscopy (Leica, Mode No. Wild M10) and the observations by cryogenic scanning electron microscopy were performed with JOEL JSA-840A following the same procedure as Michihiro did(10).

RESULTS AND DISCUSSION

It is well known that on cooling from a melt, CSA solidifies at the melting point to form α -phase liquid crystal. On further cooling, it undergoes a transition to β - or γ - phase. When the phase transition occurs, the transition points and the melting points of CSA vary with the compositions of fatty alcohols and the water content(11-15).

In the experiments with mixtures of CSA and water, we gained two peaks. The first big peak appeared at 54.4°C and the second small peak at 12.5°C. As Shoji Fukushima stated in the experiment of CSA - water mixtures(15), it is obvious that the first peak reveals the enthalpy change for liquid to α -phase transition and the second peak is for α -phase to β - or γ - phase.

Fig.1 shows the enthalpy changes at the melting points of the CSA-water mixtures plotted against the water contents. In the range below 5% water content, the ΔH values increase sharply with an increasing water content while above 5% they are directly proportional to the water content.

Brooks and Alexander reported that the formation of the strong hydrogen bonding network of hydroxy groups occurs between two alcohol and one water

molecules(16). If the formation of the hydrogen bonding between two alcohol and one water molecules occurs, the theoretical bound water content will be 3.4%. When we see the results that below 5% ΔH is not proportional to the increasing water content in Fig.1, but above 5% is proportional to that, it is believed that the formation of hydrogen bonding affects the enthalpy change and the further addition of water does not contribute ΔH any more.

The extrapolated line intersects the enthalpy axis at 33.5cal/g

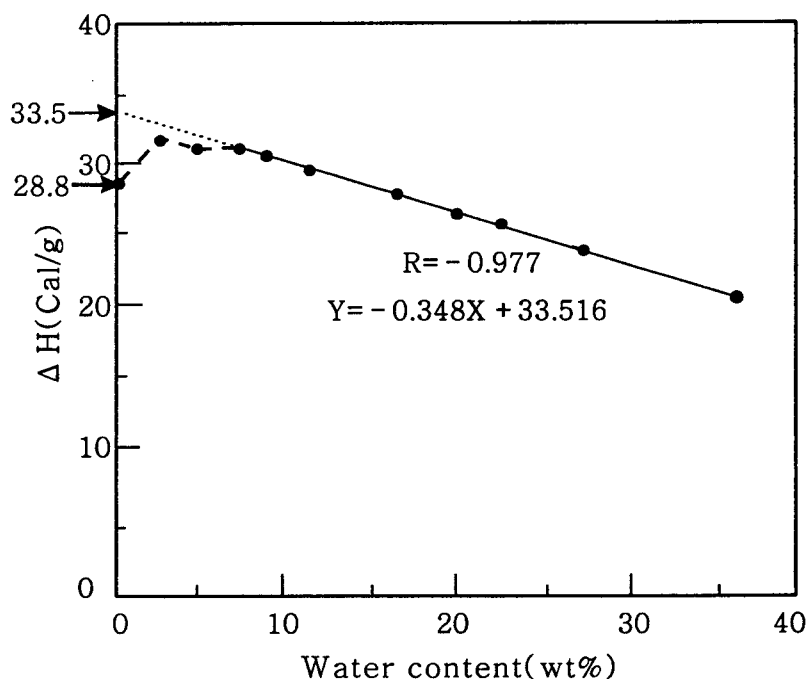


Fig. 1 Enthalpy changes at the melting point of the alkyl chains in cetostearyl alcohol/water mixtures plotted against the water content. Cooling rate 1°C/min.

showing the 4.7cal/g difference between ΔH values of sufficiently hydrated and dry CSA. It is thought that the strong network between hydroxyl groups of CSA and water may make the transformation of hydrocarbon chains difficult and result the increased ΔH between hydrated and dry CSA.

In the experiment with the mixtures of stearyl alcohol and water, the same tendency was shown ; 31.03cal/g for dry stearyl alcohol and 35.0cal/g for

sufficiently hydrated stearyl alcohol (Figure is not shown here).

In Fig.2, the dashed line represents the theoretical values of the melting enthalpy obtained from the half of the enthalpy value of the pure

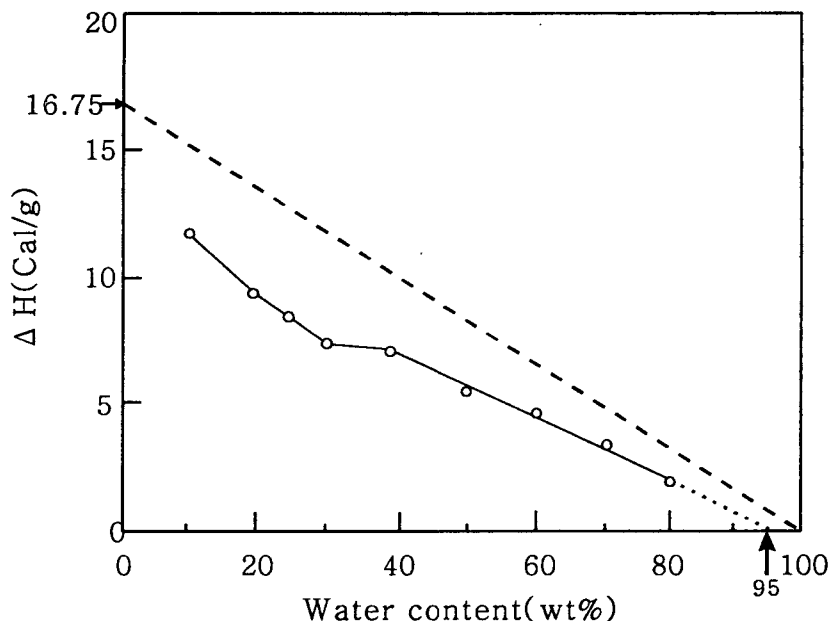


Fig. 2 Enthalpy changes at the melting temperature of the lipophilic layers in the ternary systems (POE₁₅OE/CSA/Water) at various water contents. The dashed line represents the theoretical value obtained from half of the melting enthalpy of the pure hydrated cetostearyl alcohol. Cooling rate 1°C/min

hydrated CSA because the ratio of POE₁₅OE : CSA is 1 : 1(wt%) for all samples assuming that the alkyl chains of POE₁₅OE do not contribute the melting enthalpy changes of the ternary system at all and the absolute value of the enthalpy change is directly proportional to the hydrocarbon concentration.

The ΔH values are always lower than those of the pure hydrated CSA and the values are not proportional to the varying water content up to 40%. It suggests that the addition of water influences the ΔH of the lipophilic layer below 40% water, but does not above 40% water.

It has been shown that two water molecules bind tightly per oxyethylene unit

and do not freeze upon cooling to -60°C (17,18). Therefore, we can calculate the maximum bound water content of the ternary system theoretically from the sum of bound water of CSA and POE₁₅OE ; 3.4% for CSA and 36.8% for POE₁₅OE. The maximum bound water content of the POE₁₅OE-CSA-Water ternary system can be obtained from the half of each value if we assume that POE₁₅OE and CSA molecules are arranged homogeneously forming the layers. The value will be 20.1% and the hydration of the ternary system should be completed at 20.1%. Fig.2 reveals that the further addition of water above 20.1% still contribute the enthalpy change of the lipophilic layer.

Let us consider that 20.1% water will be consumed for the bound water, and the further addition of water will exist in the hydrophilic layers of the lamellar structure formed by CSA and POE₁₅OE and make the condensed oxyethylene units extended more and more. They will become free more and more by the further addition of water and consequently reduce the attractive forces between the adjacent hydrocarbon chains. It appears that this phenomenon will continue probably until the sufficient freedom of the oxyethylene units is obtained around 40%.

We found through the microscopic and SEM observations that below and above 40% the phase was changed from the lamellar structure to the emulsion droplets (Fig.3 and 4). The phase at 30% water content was observed through a microscope and the cryo-SEM. This opaque semisolid phase showed optical anisotropy and its texture was Mosaic which is characteristic of the lamellar type liquid crystal and multilayers. Although the appearance of the sample at 70% water content looks like an ordinary emulsion, all droplets show optical anisotropy possessing a multilamellar structure like onion rings.

There is one thing in Fig.2 that we should not overlook. The

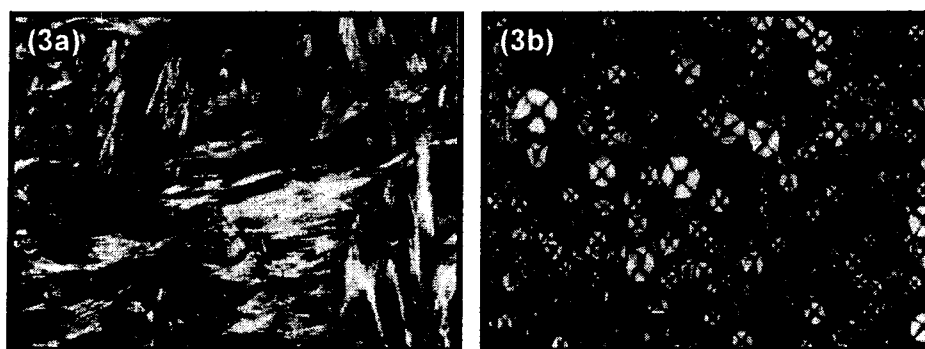


Fig. 3 Photographs obtained under polarized light with samples of Fig. 2 containing 30%(3a) and 70%(3b) water. Magnification $\times 320$.

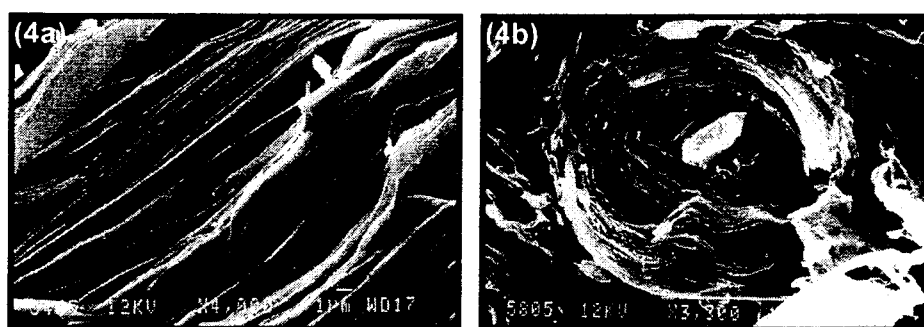


Fig. 4 Cryogenic scanning electron micrographs obtained by freezing, fracturing and etching the samples of Fig. 2 containing 30%(4a) and 70%(4b) water. Magnification $\times 4000$ (a), $\times 3300$ (b).

extrapolated line should intersect the zero ΔH at 100% water content because all samples in the tested water content were not micellar solutions. But it intersects the axis at 95% water content. It is likely that POE₁₅OE favors forming micelles partly at the high water content due to an elbow structure that may not be easy to be incorporated into the lamellar gel structure(19). For this reason, a part of POE₁₅OE not to be incorporated into the structure may form the micelles which can

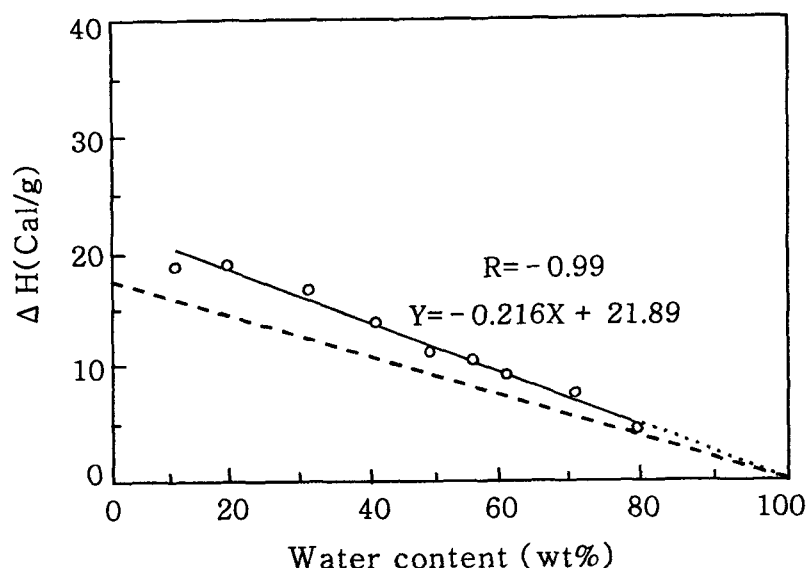


Fig. 5 Enthalpy changes at the melting temperature of the lipophilic layers in the ternary systems (POE₁₅SE/CSA/water) at various water contents. The dashed line represents the theoretical value obtained from half of the melting enthalpy of the pure hydrated cetostearyl alcohol. Cooling rate 1 °C/min

solubilize CSA partially.

In contrast to the POE₁₅OE-CSA-Water system, the ΔH values of the alkyl chains of all samples in the POE₁₅SE-CSA-Water system are higher than those of the pure hydrated CSA obviously due to an effect of the incorporation of alkyl chains of POE₁₅OE into the hydrocarbon layers (Fig. 5). It will be occurred because the total amount of hydrocarbon chains is increased as a result of the incorporation of the stearyl chains into the layers. The enthalpy changes of the alkyl chains of the POE₁₅SE-CSA-water system are directly propotional to the varying water content and we could not find a distint deviation in the ΔH in the range from 10 to 80% water content showing that the hydration of POE₁₅SE affects little the ΔH of the hydrocarbon layers of the POE₁₅SE-CSA-Water system.

The extrapolated line in Fig. 5 intersects the point close to the zero ΔH at 100% water content, and it appears that most of the stearyl chains are incorporated

in the lamellar gel structure instead of forming micelles. And the extrapolated line passes through the y axis at 21.89cal/g showing the increased ΔH by 5.12 cal/g, compared with the ΔH represented by the dashed line. This increased ΔH is believed to come from the maximum effect of the contribution of stearyl alcohol to the hydrocarbon layer. It will be necessary to compare this increased ΔH with the ΔH which can be obtained from the experiments of hydrated CSA and stearyl alcohol respectively to confirm if most of the stearyl chains are incorporated indeed in the hydrocarbon layers of CSA as we mentioned above.

Table 1 shows the values of ΔH of hydrated CSA and stearyl alcohol, hydrocarbon chains in POE₁₅SE, and 50% CSA+ 50% POE₁₅SE. The ΔH values of CSA and stearyl alcohol were obtained from the experiments, and the ΔH value for the hydrocarbon chains in POE₁₅SE was calculated considering that POE₁₅SE includes about 27% stearyl alcohol by molecular weight. Thus, the ΔH value of the mixture (CSA : POE₁₅SE = 1 : 1) can be calculated from those values.

The calculated ΔH is 21.50cal/g and the experimental ΔH from Fig.5 is 21.89cal/g. Both values are very close. It can be considered by the above results that most of molecules of POE₁₅SE are incorporated in the layers in the range of 10% to 80% water content.

From the results obtained from Fig.2 and 5, it is thought probably that the oleyl chain distorts the alkyl chains in the lamellar gel structure more than the stearyl chain, and the structure of the alkyl chains of surfactants plays the most important role in the ΔH of the lipophilic layer. And also, the effect of the hydration degree of the oxyethylene units can

Table I. Enthalpy changes of various compositions

Compositions	Enthalpy change(cal/g) (at liquid- α transition point)
CSA	33.54
Stearyl alcohol	35.00
Hydrocarbon chains	9.45
in POE ₁₅ SE(about 27%)	(35 \times 0.27)
50% CSA + 50% POE ₁₅ SE	21.50

be negligible because even in the POE₁₅OE-CSA-Water system the enthalpy changes below 40% water content is mainly resulted from an effect by the structure of the oleyl chain.

Fig.6 shows that the ΔH of the alkyl chains in the surfactant- CSA-Water ternary systems containing 15% CSA varies with the increasing concentrations of surfactants. In both systems, the ΔH is directly proportional to the increasing concentrations of surfactants ; the ΔH increases in the POE₁₅SE -CSA-Water systems and decreases in the POE₁₅OE-CSA-Water systems revealing a similar tendency to the results shown in Fig.2 and 5. We can say that the incorporation of surfactants into the lamellar gel structure leads to the increased ΔH in the case of the POE₁₅SE-CSA-Water systems and the decreased ΔH in

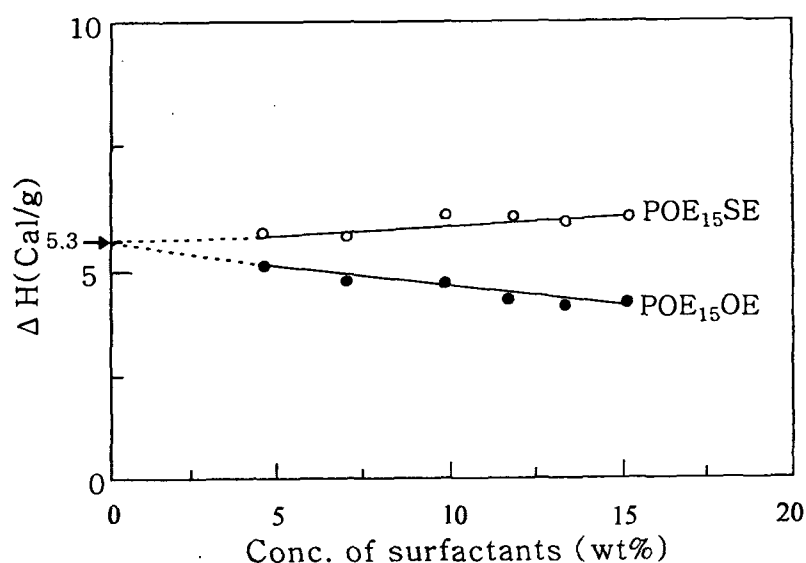


Fig. 6 Enthalpy changes of the alkyl chains in the ternary systems (Surfactant/CSA/Water) containing 15% cetostearyl alcohol with increasing concentrations of surfactants (○: POE₁₅SE. ●: POE₁₅OE). Cooling rate 0.5°C/min.

the POE₁₅OE-CSA-Water systems to the contrary.

It is well known that emulsions are unstable thermodynamically and are broken down in the end. If the ternary systems under the investigation here become unstable and their deteriorations are resulted from the breakdown of the lamellar gel structure, that is to say, the separation into each component, the total ΔH should be increased for the POE₁₅OE-CSA-Water system and decreased for the POE₁₅SE-CSA-Water system in the light of the results of Fig.6 since the systems below 15% concentrations of POE₁₅OE and POE₁₅SE in water exist only as micellar solutions which can not contribute ΔH at all. In this sense Fig.6 offers important information for the estimation of the stability of the concerned ternary systems and we will discuss it more later.

In Junginger's study performed with a nonionic surfactant (polyoxyethylated-20-glycerol-monostearate : PGM20) - cetostearyl alcohol - water system, he stated that the system was consisted of four phases ; mixed crystals of PGM20 and

cetostearyl alcohol (hydrophilic gel phase), a lipophilic phase (predominantly cetostearyl alcohol), a dispersed lipophilic phase (inner oil phase), and bulk water phase (20). In other words, two different type crystals coexist with a dispersed lipophilic phase in the bulk water phase. One is the well mixed crystals of PGM 20 and cetostearyl alcohol, and the other is the crystals consisted of hydrated cetostearyl alcohol predominantly. If so, the ratios of two crystals may vary depending on the ratios of surfactants and cetostearyl alcohol.

We varied the ratios of POE₁₅OE : CSA and POE₁₅SE : CSA, and examined the ΔH by DSC after one week storage of samples at 25°C (Fig. 7). In both Fig.7 (A) and (B), the main endothermal peak was observed at 55°C when the ratio of CSA was high. Another peak was appeared at 45°C for (A) and at 61°C for (B) with the increased concentrations of surfactants.

The peaks observed at the high ratios of CSA resembled the one of hydrated CSA which was also observed at 55°C (see a below right corner in Fig. 7 (A)). As the ratios of the surfactants were increased, however, the second peaks appeared and grew while the main peaks at 55°C became smaller. When we compare these peaks with Junginger's statement(20), it can be said that the main peak at 55°C may represent a lipophilic gel phase(predominantly CSA) and the second peaks at 45°C and 61°C respectively probably represent the mixed crystals (hydrophilic gel phase) of surfactants (POE₁₅OE and POE₁₅SE) and CSA. If we take a look at Fig. 7(A) and (B), we can recognize that POE₁₅SE-CSA-Water

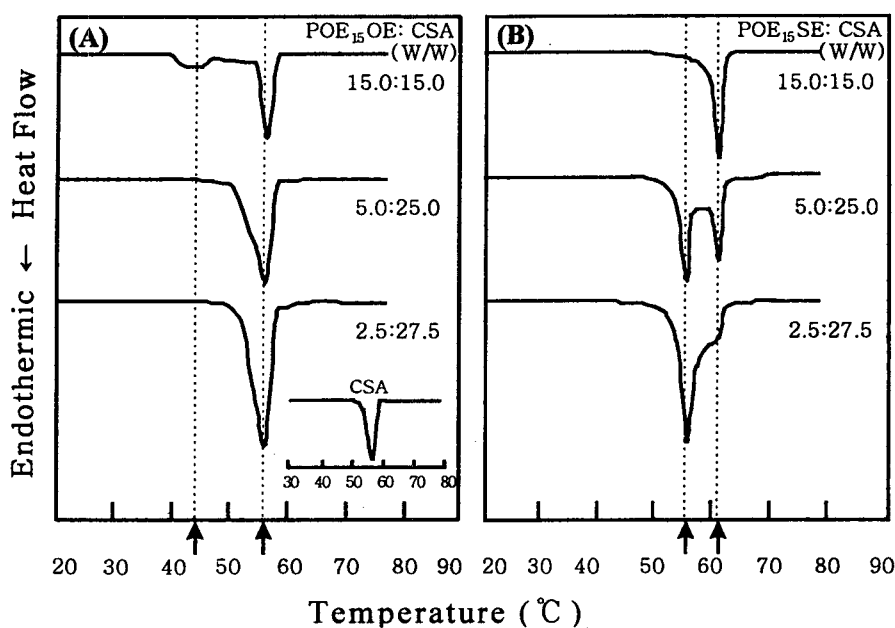


Fig.7 DSC thermal profiles of surfactant/CSA/water ternary systems containing 70% water with the varying ratios of surfactants and CSA. (A): POE₁₅OE/CSA/water, (B): POE₁₅SE/CSA/water. Heating rate 1°C/min.

system possesses more mixed crystals than POE₁₅OE-CSA-water does at the same ratio of surfactant and CSA. These mixed crystals consist of POE₁₅OE or POE₁₅SE and CSA, and such lamellar mixed crystals can swell in dependence of the total water content and the length of oxyethylene unit. The hydrophilic gel phase forms a three-dimensional network and represents the coherent gel together with the aqueous water phase, while the lipophilic gel phase is able to crystalize in separate crystals(20). Thus, the stabilities of the ternary systems may depend on the hydrophilic gel phase.

Finally, we investigated the stabilities of two ternary systems under the long-term storage at -15°C, 0°C, and 25°C by the measurements of

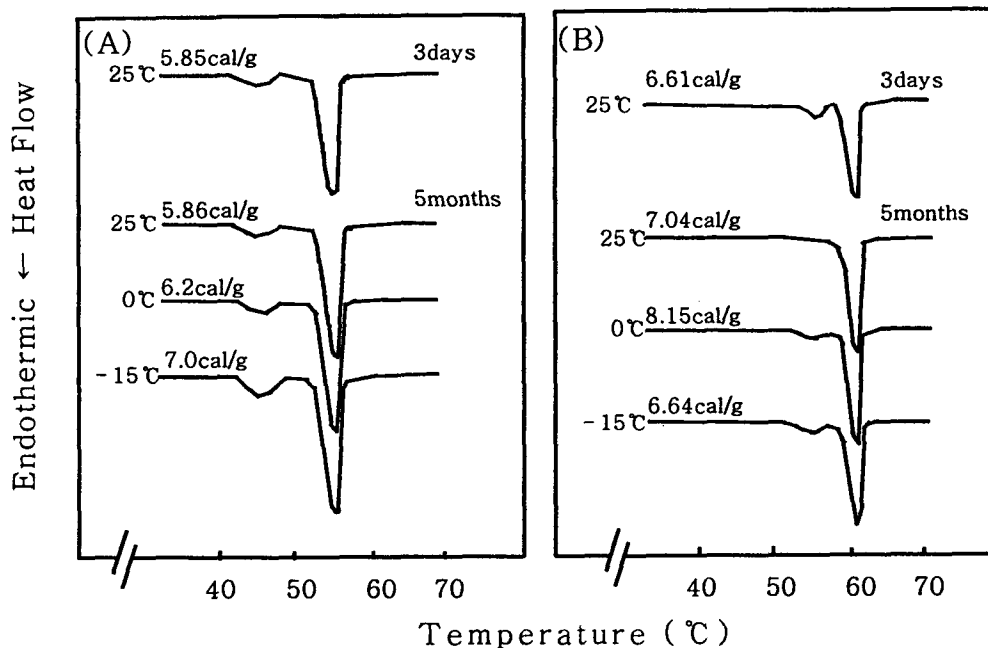


Fig.8 DSC thermal profiles of surfactant/CSA/water ternary systems containing 20% CSA and 10% surfactant after storage at 25°C, 0°C, and -15°C for stated times. (A): POE₁₅OE/CSA/water, (B): POE₁₅SE/CSA/water. Heating rate 1°C/min.

ΔH (Fig.8).

As we mentioned previously, the total enthalpy changes of the systems should be calculated from the sum of the areas of two peaks because two different type crystals can coexist in the systems in a certain ratio of surfactant and CSA. In the POE₁₅OE-CSA-Water systems, the total enthalpy changes will be increased and the peak at 55°C will grow up if the systems have been deteriorated. But in the POE₁₅SE-CSA-Water systems, the total ΔH will be decreased showing the grown peak at 55°C if so (refer to Fig. 6).

Fig.8 (A) shows that the peaks at 55°C of the samples consisted of 20% CSA and 10% POE₁₅OE, and stored at the different temperatures (-15°C, 0°C, and 25°C) for 5 months became bigger than that of the initial sample leading to the increased total ΔH. Fig. 8(B) having the same concentration compositions as Fig. 8(A) reveals that the peaks at 55°C became smaller or disappeared, and the total ΔH was

increased.

For the POE₁₅OE-CSA-Water systems, the results obtained here agree well with our expectation that the total ΔH will be increased on the way of the deterioration of the system. But if the POE₁₅SE-CSA-Water systems have been deteriorated, the total ΔH should be decreased instead of showing the increased ΔH .

If we take a close look at the peaks at 55°C in Fig.8(B), we may be able to find out the reason. After 5 months, the peaks at 55°C were disappeared or became smaller. One may think that those phenomena were resulted from CSA solubilized partially by free micelles during storage, but it is not reasonable because the micellar solutions can not contribute the enthalpy change and the total ΔH should be decreased accordingly. Instead, it may be more reasonable that molecules of hydrated CSA might be transferred for more participation in the mixed crystal phase bringing the increased hydrocarbon content.

Fig. 9 represents the photos of the samples of Fig. 9 (A) and (B) after 5month storage at 25°C. Fig. 8(A) was the sample of the POE₁₅OE-CSA-Water system and separated into the two phases. In the mean time, the sample of the POE₁₅SE-CSA-Water system(Fig.9(B)) did not show any separations. G.M.Eccleston mentioned that the appearances and rheological stabilities of the emulsions were related closely to the stabilities of viscoelastic networks formed in the continuous phases when aqueous surfactant solution interacted with long chain alcohol(21). From G.M. Eccleston's viewpoint and our results, it is obvious that POE₁₅OE will not make stable emulsions due to the poor ability for the formation of the

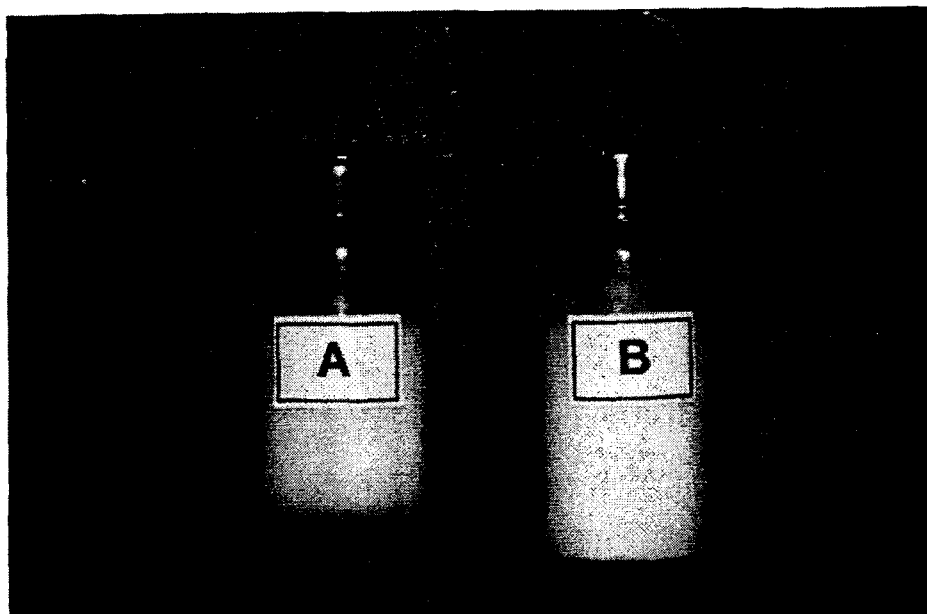


Fig.9 Photographs illustrating the breaking of the sample of Fig. 8(A) and the stabilized state of the sample of Fig.8(B) after 5 month storage at 25°C.

hydrophilic gel phase, which is caused by the elbow structure of oleyl alcohol.

CONCLUSIONS

It has been reported by many authors that the emulsion deteriorations are progressed through a complicated process, but it was not easy to understand the those processes clearly. And also there are not many proper methods for the determinations of the relationship of the phase changes in emulsions and their stabilities. In this point, the results obtained from this study may help them to understand and study the emulsion deteriorations more specific, especially the relationship between two different type crystals on the stabilities of emulsions.

It is concluded that POE₁₅SE-CSA-Water systems are more stable than POE₁₅OE-CSA-Water systems during storage and the main cause is from the alky chain structure of surfactants, and the measurements of ΔH by DSC can be used as

increased.

For the POE₁₅OE-CSA-Water systems, the results obtained here agree well with our expectation that the total ΔH will be increased on the way of the deterioration of the system. But if the POE₁₅SE-CSA-Water systems have been deteriorated, the total ΔH should be decreased instead of showing the increased ΔH .

If we take a close look at the peaks at 55°C in Fig.8(B), we may be able to find out the reason. After 5 months, the peaks at 55°C were disappeared or became smaller. One may think that those phenomena were resulted from CSA solubilized partially by free micelles during storage, but it is not reasonable because the micellar solutions can not contribute the enthalpy change and the total ΔH should be decreased accordingly. Instead, it may be more reasonable that molecules of hydrated CSA might be transferred for more participation in the mixed crystal phase bringing the increased hydrocarbon content.

Fig. 9 represents the photos of the samples of Fig. 9 (A) and (B) after 5month storage at 25°C. Fig. 8(A) was the sample of the POE₁₅OE-CSA-Water system and separated into the two phases. In the mean time, the sample of the POE₁₅SE-CSA-Water system(Fig.9(B)) did not show any separations. G.M.Eccleston mentioned that the appearances and rheological stabilities of the emulsions were related closely to the stabilities of viscoelastic networks formed in the continuous phases when aqueous surfactant solution interacted with long chain alcohol(21). From G.M. Eccleston's viewpoint and our results, it is obvious that POE₁₅OE will not make stable emulsions due to the poor ability for the formation of the

13. Tasumi, M., Shimanouchi, T., Watanabe, A., and Goto, R., *Bull. Inst. Chem Res., Kyoto Univ.* 20, 629 (1964).
14. A. S. C. Lawrence, M. A. Al-Mamun, M. P. McDonald, *Trans. Faraday Soc.*, 63, 2789 (1967).
15. Shoji Fukushima and Michihiro Yamaguchi, *Yukagak*, 29, 933 (1980).
16. Brooks, J. H. and Alexander A. E., *J. Phys. Chem.*, 66, 1851 (1960).
17. Hager SL, Macurry TB, *Ja Appl. Polym. Sci.*, 25, 1559 (1980).
18. T. de Vringer, J. G. H. Joosten, and H. E. Junginger,
19. S. E. Friberg, *J. Soc. Cosmet. Chem.*, 41, 155-171 (1990).
20. Junginger, H. E., *Dtsch. Apoth. Ztg.*, 131, 1933-1941 (1991).
21. G. M. Eccleston, *J. of Colloid and Interface Sci.*, 57(1), 66 (1996).