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# Phase diagrams of surfactant/water/synthetic perfume ternary systems

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*Abstract*: The phase diagrams of hexadecyl polyoxyethylene ether ($C_{16}POE_{10}$)/water/synthetic perfume, and sodium dodecyl sulfate (SDS)/water/synthetic perfume ternary systems were prepared. The synthetic perfumes used are, d-limonene, α-hexylcinnamaldehyde, α-ionone, benzyl acetate, linalool, and eugenol. In a series of $C_{16}POE_{10}$/water/synthetic perfume ternary systems, as the hydrophilicity of synthetic perfume increases, the regions of normal and inverse micellar solution phases were found to be extended, while that of the lamellar liquid crystal phase was reduced. Moreover, every region of normal micellar solutions, inverse micellar solutions, and lamellar liquid crystal phases in SDS/water/synthetic perfume ternary systems was found to be smaller than those in $C_{16}POE_{10}$/water/synthetic perfume systems.

*Key words*: Surfactant – perfume – lamellar liquid crystal – phase diagram – inorganic/organic value

## Introduction

One of the most prominent characteristics of a concentrated ternary system of amphiphilic compounds, water, and oily materials shows various kinds of phases, e.g., coagel, gel, or liquid crystal, depending on temperature and composition. Thus, the effect of amphiphilic compounds upon the characteristics of a concentrated ternary system have been detailed, both experimentally and theoretically [1–8]. In these previous discussions, however, common chemical compounds such as saturated-hydrocarbon, alcohol, and ether have also been adopted as the oil bearing component, but few synthetic perfumes have been discussed.

Recently, concentrated solutions occurring in surfactant/water/oily material ternary systems are used in many practical applications. In the field of modern cosmetics, many preparations produced by liquid crystal or gel formed in a ternary system have been produced, and synthetic perfumes are usually added to such preparations [9–11]. Hence, understanding how surfactants interact with synthetic perfumes in a concentrated solution is essential for industrial applications of surfactants.

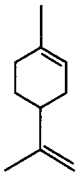
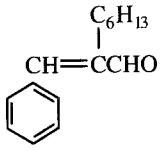
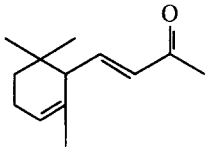
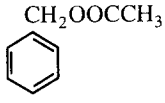
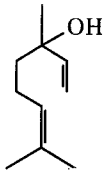
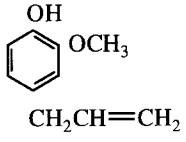
In investigating surfactant/water/oily material concentrated ternary systems, it is necessary to determine their phase equilibrium diagrams. In this paper, we investigate the phase diagrams of hexadecyl polyoxyethylene ether/water/synthetic perfume and sodium dodecyl sulfate/water/synthetic perfume ternary systems and discuss the interaction between surfactants and synthetic perfumes in relation to variations in phase regions, especially of normal micellar solutions, inverse micellar solutions, and lamellar liquid crystal phases.

## Experimental

### *Materials*

Nonionic surfactant, hexadecyl polyoxyethylene ether ($C_{16}POE_{10}$; $C_{16}H_{33}O(CH_2CH_2O)_{10}H$),

Table 1. Chemical structure, molecular weight, and purity of synthetic perfumes used

| Chemical structure | Synthetic perfume | Abbreviation | M.W. | Purity |
|---|---|---|---|---|
|  | d-Limonene | LN | 136.24 | > 95% |
|  | α-Hexylcinnamaldehyde | HCA | 216.33 | > 95% |
|  | α-Ionone | IN | 192.30 | > 95% |
|  | Benzyl acetate | BA | 150.17 | > 98% |
|  | Linalool | LL | 154.25 | > 98% |
|  | Eugenol | EL | 164.21 | > 98% |

was supplied by Nihon Surfactant Industries Co., Ltd., Tokyo, Japan. This has a narrow molecular weight distribution. The purity of this surfactant was ascertained from surface tension measurements and differential scanning calorimetry.

The anionic surfactant, sodium dodecyl sulfate (SDS), was the purest grade product ( > 99.7% purity) produced by Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. It was recrystallized from ethanol and extracted with ether.

Synthetic perfumes, d-limonene (LN), α-hexylcinnamaldehyde (HCA), α-ionone (IN), benzyl acetate (BA), linalool (LL), and eugenol (EL) were supplied by Hasegawa Kouryo Co., Ltd., Tokyo, Japan, and were used without further purification. Their chemical structures, molecular weights, and purities are shown in Table 1. In addition, the ratio between the inorganic value of the functional groups (I) and organic values of the functional groups (O) of organic molecules, which is the I/O value proposed by Fujita [12, 13], was applied to define the hydrophilicity of the perfumes [14]. The resulting I/O values of the perfumes were LN; 0.07, HCA; 0.27, IN; 0.30,

BA; 0.42, LL; 0.52, and EL; 0.69, respectively, indicating an increase in I/O values with an increase in their hydrophilicity. Moreover, it has also been found by Fujita that substances involving similar I/O values have strong affinity to dissolve with each other [12, 13, 15].

Water used in the experiments was twice distilled and was deionized with an ion-exchanger (NANO pure D-1791 of Barnstead Co., Ltd.) and then distilled again just before use; its resistivity was about 18.0 MΩ·cm and pH was 6.7.

### *Method*

*Preparation of a concentrated surfactant solution.* A given amount of surfactant, a synthetic perfume, and water were placed in several test tubes which were then sealed. The mixtures were gently warmed at about 80 °C and stirred until homogenized with a vibrator. Then, the mixtures were allowed to attain equilibrium over a period of 2–3 days at 30 °C, and the appearance of the phase in these tubes was observed. After these first observations were carried out, their appearance was again re-examined several days later, when no change in the phase was detected.

*The determination of a phase diagram.* The appearance and fluidity of the sample were observed with the naked eye. The presence of a liquid crystal phase in the solution was detected with a polarized filter and identified under a microscope with polarized light by comparing the textures with those of photomicrographs in the literature [16, 17]. The measurements and determination were made at 30 °C.

## Results and discussion

*Phase diagrams of nonionic surfactant/water/synthetic perfume ternary systems.* The phase diagrams for $C_{16}POE_{10}$, water, and synthetic perfume (LN, HCA, IN, BA, LL, and EL) ternary systems are shown in Figs. 1, 2, 3, 4, 5, and 6, respectively. In these figures, a variety of phases was observed: $L_1$ and $L_2$; isotropic liquid solution phases, $LC_h$ and $LC_l$; liquid crystal phases, VI; viscous isotropic solution phase, S, and a phase including a crystalline surfactant in equilibrium with other kinds of phases. Finally, the unmarked

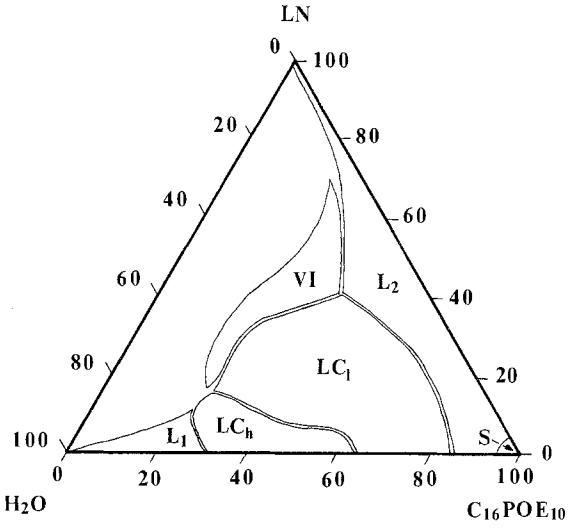



Fig. 1. Phase diagram for $C_{16}POE_{10}$/water/LN ternary system at 30 °C. The concentrations are given in weight fractions

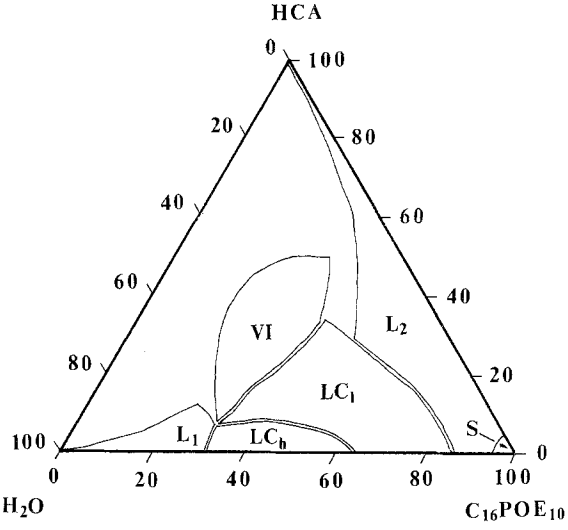



Fig. 2. Phase diagram for $C_{16}POE_{10}$/water/HCA ternary system at 30 °C. The concentrations are given in weight fractions

area to the left in these diagrams corresponds to a variety of multiphase regions. A similar tendency is recognized in the results for hexadecyl polyoxyethylene ether, water, and *n*-hexanol ternary systems [18].

$L_1$ emanating from the pure water corner appears where a synthetic perfume has been solubilized by $C_{16}POE_{10}$ normal micelle [18–20].

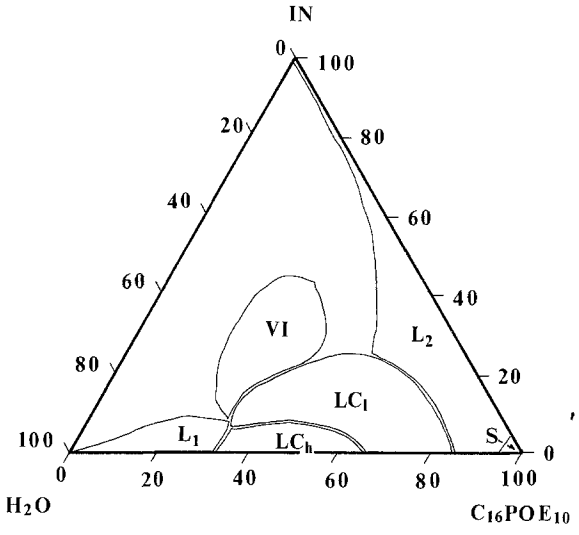



Fig. 3. Phase diagram for $C_{16}POE_{10}$/water/IN ternary system at 30 °C. The concentrations are given in weight fractions

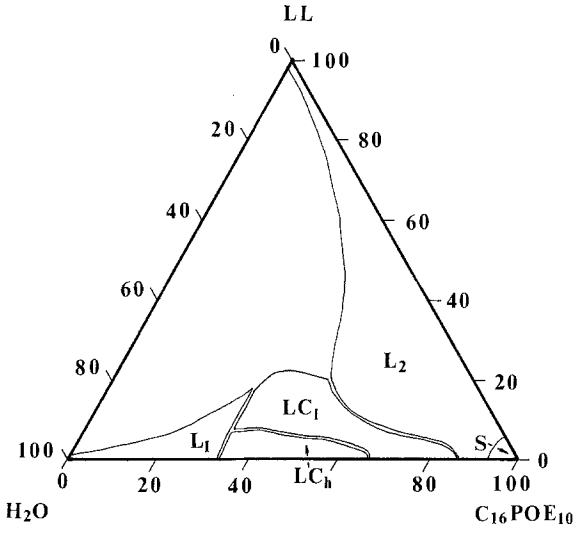



Fig. 5. Phase diagram for $C_{16}POE_{10}$/water/LL ternary system at 30 °C. The concentrations are given in weight fractions

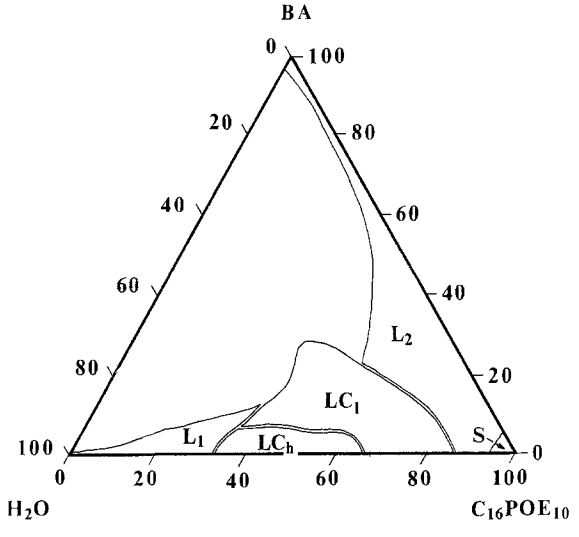



Fig. 4. Phase diagram for $C_{16}POE_{10}$/water/BA ternary system at 30 °C. The concentrations are given in weight fractions

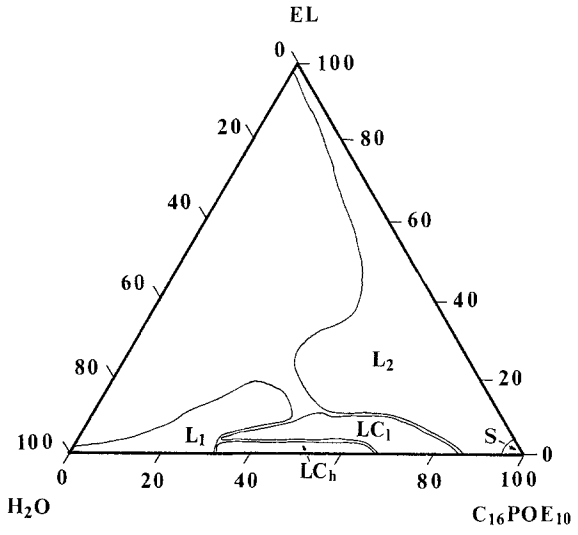



Fig. 6. Phase diagram for $C_{16}POE_{10}$/water/EL ternary system at 30 °C. The concentrations are given in weight fractions

As can be seen from these diagrams, the region of $L_1$ gradually increases with the hydrophilicity of the synthetic perfume. This finding suggests that the hydrophilic synthetic perfume is solubilized into a normal micelle more readily than the hydrophobic synthetic perfume. This tendency is also observed in our previous study on the solubilization of synthetic perfumes with a dilute aqueous surfactant solution [21, 22].

$L_2$ has been obtained at higher concentrations of surfactant in the right-hand section of these diagrams. While synthetic perfume is a solubilizate and water a solvent in $L_1$, the reverse is the case with $L_2$. That is, $L_2$ is where the inverse

micelle solubilizing water exists in a synthetic perfume solvent [18–20]. As these diagrams show, in analogy with $L_1$, the $L_2$ region also increases because of the rise in the hydrophilicity of the synthetic perfume.

The regular solution theory represents that the affinity between a solute and a solvent increases with a decrease in the heat of dissolution in the binary system. Moreover, the heat of dissolution is proportional to the difference between the I/O values of the solute and of the solvent. Thus, the smaller the difference between the I/O values of the compounds, the greater the affinity to dissolve with each other [12, 13, 15]. It can be postulated that the I/O value of $C_{16}POE_{10}$ corresponds to 1.13 from Fujita's method, the affinity between $C_{16}POE_{10}$ and a perfume increases with an increase in the I/O value of the perfume, and the regions of $L_1$ and $L_2$ become enlarged with an increase in the hydrophilicity of the perfume as shown in these diagrams.

$L_1$ at an increased surfactant concentration is transferred into two distinct liquid crystals, $LC_h$ and $LC_l$. $LC_h$ has a structure of close-packed cylinders, while $LC_l$ is a well-known lamellar structure. Observation under polarized light confirms the structure of $LC_h$ and $LC_l$, the patterns of "angular texture" and "mosaic texture" for the hexagonal and the lamellar liquid crystals, respectively [16, 17].

It is found in these diagrams that both the liquid crystal regions significantly decrease with an increase in the hydrophilicity of synthetic perfumes, in contrast to $L_1$ and $L_2$. Furthermore, maximum concentrations of each synthetic perfume which can form a stable lamellar structure simultaneously become diminished. Thus, hydrophobic synthetic perfumes yield lamellar structures with more pronounced stability (than hydrophilic synthetic perfumes) until reaching their higher concentrations.

Winsor reported initially that the variation of dispersing tendencies for an amphiphilic compound/water/oily material ternary system was expressed qualitatively [23]. He concluded that the phase variation in the ternary system was influenced by the $R$ value, corresponding to the ratio between the cohesive interaction energies of an amphiphilic compound with an oil region ($A_{co}$) and an aqueous region ($A_{cw}$). Furthermore, Bourrel [24] modified and extended Winsor's original $R$-theory, defined as the following ratio;

$$R = \frac{A_{co} - A_{oo} - A_{ll}}{A_{cw} - A_{ww} - A_{hh}}, \quad (1)$$

where $A_{oo}$ is the cohesive energy between molecular oils, $A_{ww}$ is the cohesive energy between molecular water, $A_{ll}$ is the cohesive energy between surfactants caused by their lipophilic portions, and $A_{hh}$ is the cohesive energy between surfactants caused by their hydrophilic portions. When the $R$ value in Eq. (1) is just equivalent to unity, a lamellar liquid crystalline (or bicontinuous) structure can be found in the surfactant/water/oily material ternary system [25–27].

It can be postulated from Eq. (1) that $A_{cw}$, $A_{ww}$, $A_{hh}$, and $A_{ll}$ in Eq. (1) are independent of the properties of a synthetic perfume. In contrast to them, since $C_{16}POE_{10}$ has a stronger affinity to hydrophilic perfume than to hydrophobic perfume, the term $A_{co}$ with hydrophilic perfume becomes greater than that with hydrophobic perfume. Moreover, hydrophilic perfumes such as EL and LL probably give a large $A_{oo}$ because of intermolecular attraction with the hydroxyl group in their molecular structure.

These suggestions provide that $A_{co}$ and $A_{oo}$ in the ternary systems including the hydrophilic perfume become too large for the $R$ values to be equal to unity. The region of $LC_l$, therefore, decreases markedly as hydrophilic property of the perfume increases.

*The comparison between the phase diagrams of anionic and nonionic surfactants.* Now, in order to define whether there is a distinction of phase diagrams between anionic and nonionic surfactants, the above phase diagrams in which the more hydrophilic perfume, EL, and the less hydrophilic perfume, LN, are treated are modified by replacing $C_{16}POE_{10}$ with SDS. Figures 7 and 8 express SDS/water/LN and SDS/water/EL ternary systems, respectively, where the symbols follow the diagrams above. The difference in the influence of anionic and nonionic surfactants on the variation of phase regions can be obtained from the comparison between the $C_{16}POE_{10}$ (Figs. 1 and 6) and the SDS (Figs. 7 and 8) ternary systems.

The $L_1$ region where EL is solubilized with a normal micelle is decreased by exchanging $C_{16}POE_{10}$ for SDS, while the variation of the $L_1$

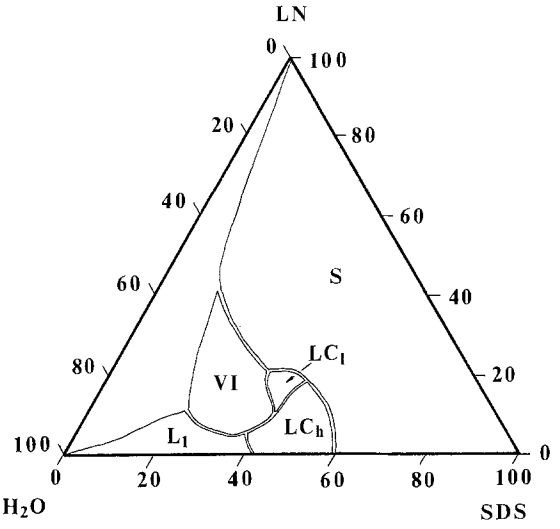



Fig. 7. Phase diagram for SDS/water/LN ternary system at 30 °C. The concentrations are given in weight fractions

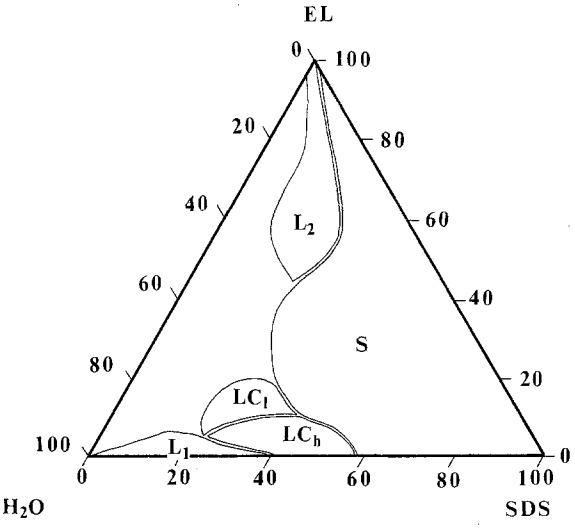



Fig. 8. Phase diagram for SDS/water/EL ternary system at 30 °C. The concentrations are given in weight fractions

region with the normal micelle solubilizing LN is almost independent of the substitution. This suggests that $C_{16}POE_{10}$ is superior to SDS with regard to the solubilization of EL, and that the effect of SDS on the solubilization of LN is almost equal to that of $C_{16}POE_{10}$.

The effect of the replacement of $C_{16}POE_{10}$ with SDS on the variation of the $L_2$ region is much greater than on that of the $L_1$ region. The $L_2$ regions in the SDS/water/synthetic perfume ternary systems are much smaller in size when compared with those in the $C_{16}POE_{10}$/water/synthetic perfume ternary systems. In particular, the $L_2$ phase in the SDS/water/LN ternary system is not recognized at all.

Furthermore, the regions of both the liquid crystal phases, $LC_h$ and $LC_l$, are reduced and are scarcely formed at the higher synthetic perfume content on exchanging $C_{16}POE_{10}$ for SDS. These phenomena indicate that it is difficult to form a lamellar liquid crystal structure in the SDS/water/synthetic perfume ternary systems.

As well as in the case of $C_{16}POE_{10}$/water/synthetic perfume ternary systems, the reduction in the $L_1$ and $L_2$ regions in the SDS/water/synthetic perfume ternary systems may be attributed to the lower affinity between surfactant and synthetic perfumes. Actually, the I/O value of SDS estimated by Fujita's method yields a result of more than 2.0, becoming much larger than those of synthetic perfumes. On the other hand, the I/O value of $C_{16}POE_{10}$, 1.13, is closer to the I/O values of synthetic perfumes than that of SDS. Therefore, the consideration that compounds with the same I/O values have a strong affinity for each other suggests that SDS cannot interact with either EL or LN as strongly as $C_{16}POE_{10}$; that is, the term $A_{co}$ in Eq.(1) is reduced by converting $C_{16}POE_{10}$ into SDS.

It may also be expected that this substitution yields a variation, not only in $A_{co}$, but also in $A_{cw}$ and $A_{hh}$. The fact that I/O values of SDS are larger than those of $C_{16}POE_{10}$ demonstrates that the hydrophilicity of SDS is greater than that of $C_{16}POE_{10}$, and that SDS strongly interacts with molecular water. Thereby, the term $A_{cw}$ is enhanced by converting $C_{16}POE_{10}$ into SDS. Moreover, the head groups of SDS are generally negatively charged and repulse each other, so that this substitution causes $A_{hh}$ to have large negative values [28].

These variations in $A_{co}$, $A_{cw}$, and $A_{hh}$ obtained by converting $C_{16}POE_{10}$ into SDS leads to that the $R$ value in Eq. (1) may deviate far from unity, in which case the $LC_l$ regions are extremely narrow in the SDS/water/synthetic perfume ternary systems as shown in Figs. 7 and 8.

## Conclusion

In $C_{16}POE_{10}$/water/synthetic perfume ternary systems, normal and inverse micellar solution regions are extended with an increase in the hydrophilicity of synthetic perfume, while lamellar liquid crystal regions are reduced. Moreover, it is recognized that the regions of normal micellar solutions, inverse micellar solutions, and lamellar liquid crystal phases in SDS/water/synthetic perfume ternary systems are smaller when compared with those in the $C_{16}POE_{10}$/water/synthetic perfume ternary systems. In addition, by comparing the I/O values of each compound, it may be concluded that hydrophilic synthetic perfume can interact with $C_{16}POE_{10}$ more strongly than hydrophobic synthetic perfume, and that the interaction between the synthetic perfume and $C_{16}POE_{10}$ is much larger than that between the synthetic perfume and SDS. This may be one of the most important reasons for the variation in the phase diagrams as mentioned above.

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