ORIGINAL

Solubilization of Some Synthetic Perfumes by Ionic and Non-Ionic Surfactants

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Abstract : Solubilization of the synthetic perfumes, eugenol, linalool, benzyl acetate, α -ionone, α -hexylcinnamaldehyde and *d*-limonene by the ionic surfactants, sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC) and a non-ionic surfactant such as dodecyl polyoxyethylene ethers (C_{12} POE₂₀) was investigated and assessed in terms of solubilizing capacity (SC) of the surfactants. For the same perfume, except for LN, SC followed the order, C_{12} POE₂₀>SDS>DTAC. On the other hand, the order of SC for LN was C_{12} POE₂₀>DTA>SDS. The relative importance of micelle-perfume interactions and of volume of effective solubilization site in micelle may be explanation for these findings.

Key words : solubilization, synthetic perfume, solubilizing capacity

1 Introduction

Synthetic perfumes are often used in industrial products such as cosmetics, foods, detergents, pesticides, and coating materials. The synthetic perfumes are used in various forms combined with other materials such as emulsifiers or solubilizers, depending on the properties of the medium, the solubility of the perfume in the solvent, the stability of the perfume, etc. In particular fields of cosmetic and food science, surfactants are used to solubilize oily synthetic perfumes. The aqueous solution containing perfumes solubilized by surfactants becomes transparent, and segregation of perfume molecules from the solution is prevented over a long period of time. This is preferable for the practical use of the perfumes, and hence, it is essential for many industrial applications of perfumes to understand how the perfume interacts with the surfactant in an aqueous solution. Although many papers are published concerning the solubilization of normal hydrocarbons, alcohols, and water-insoluble dry by various surfactants, few studies have been made on the solubilization of synthetic perfume compounds^{1)~5)}.

In previous paper, we have reported the solubilization of some synthetic perfumes by anionic⁶⁾, nonionic⁷⁾, and anionic-nonionic mixed surfactants^{8),9)} in aqueous solutions. These studies have suggested that the hydrophilic property of the synthetic perfume compounds is related to their *maximum additive concentration* (MAC) in surfactant solutions and *solubilizing capacities* (SC) of surfactants. It has been also revealed that perfume compounds tend to penetrate into the hydrophilic portion of the micelle ; this means that the hydrophilic head group of surfactants plays an important role on the solubilization of perfume compounds.

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In the present study, we determined the SC for typical synthetic perfumes using several types of surfactants with different hydrophilic head groups, that is, sodium dodecyl sulfate, dodecyltrimethylammonium chloride, and dodecyl polyoxyethylene ethers, and discussed the effect of the surfactant head group on the solubilization behavior for the perfumes.

2 Experimental Section

2.1 Materials. Anionic surfactant, sodium dodecyl sulfate (SDS), was the purest grade product of Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. It was recrystallized from ethanol and extracted with ether.

Nonionic surfactant, dodecyl poly(oxyethylene) ethers [$C_{12}POE_{20}$, $C_{12}H_{25}O(CH_2CH_2O)_{20}H$] was supplied by Nihon Surfactant Industries Co., Ltd., Tokyo, Japan. It has a narrow molecular weight distribution. The purity was ascertained by surface tension measurements.

Cationic surfactant, dodecyltrimethylammonium chloride (DTAC), was the purest grade product of Nacalai Tesque Co., Ltd., Kyoto, Japan. It was recrystallized three times from acetone.

Synthetic perfumes, eugenol (EL), linalool (LL), benzyl acetate (BA), α -ionone (IN), α -hexylcinnamaldehyde (HCA), and *d*-limonene (LN), were supplied by Hasegawa Kouryo Co., Ltd., Tokyo, Japan, and were used without further purification. The chemical structures, molecular weights, and hydrophilic-lipophilic balance (HLB) of the perfumes are listed in Table 1. The values of HLB of the compounds were calculated using the method of Fujita^{10)~12)}.

Table 1 Chemical Structure, Abbreviation, Molecular Weight, and HLB of Synthetic Perfumes Used in this Study.

Chemical structure	Synthetic perfume	Abbreviation	Molecular weight	HLB
Eugenol	EL	164.21	6.9
Linalool	LL	154.25	5.2
Benzylacetate	BA	150.17	4.2
α -Ionone	IN	192.30	3.0
α -Hexylcinnamaldehyde	HCA	216.33	2.7
<i>d</i> -Limonene	LN	136.24	0.7

Water used in the experiments was twice distilled and deionized with an ion-exchanger (NANO pure D-1791 of Barnstead Co., Ltd.), and distilled again prior to use. The resistivity of the water was about $18.0 \text{ M}\Omega \cdot \text{cm}$ and the pH was 6.7; the surface tension was 72.1 mN/m at 30°C .

2.2 Preparation of surfactant solutions and aqueous solutions including synthetic perfume. 20 mL portions of water or a surfactant solution with a given concentration were placed into several 100 mL glass stoppered Erlenmeyer flasks, and varying amounts of a synthetic perfume were added. The mixtures were stirred by a shaker (Model SS-82D Type of Tokyo Rikakikai Co., Tokyo, Japan) for 12h and allowed to stand for 12h to establish a solubilization equilibrium at 30°C .

2.3 Determination of maximum additive concentration (MAC) and solubility in water.

After equilibrium has been established in the solutions, the turbidities of the solutions were determined by measuring the transmittance at 700 nm with a double-beam spectrophotometer (Model MPS-2000 of Shimadzu Co., Ltd., Tokyo, Japan) with a quartz cell (10 mm light path length) as described in the previous paper^{(6)~(9)}. When the amount of a perfume added to a surfactant solution was increased, the turbidity of the solution was kept at zero up to a certain concentration of the perfume, and then increased rapidly due to the appearance of oily droplets of unsolubilized perfume. MAC was determined from the inflection point in the plot of turbidity *vs.* perfume concentration at a given surfactant concentration.

The solubilities of perfumes in water were measured by using a total organic carbon analyzer (Model TOC-5000 of Shimadzu Co., Ltd.), which determined the amount of total organic carbon in the aqueous solution. Samples for the solubility measurements were prepared by placing excess perfume in water, followed by stirring for 12h. The undissolved organic phase was removed before the measurement by utilizing a glass-filter (Glass Microfibre Filter of Whatman Ltd., England) when necessary to separate the small oily particles of the perfume from the aqueous solution.

2.4 Determination of phase diagram. A given amount of a surfactant, a synthetic perfume, and water placed in several test tubes. The appearance and fluidity of the sample were visually observed as the temperature was increased. The presence of a liquid crystal phase in the solution was confirmed with a polarized filter, and was identified under a polarized microscope by comparing the textures with those of photomicrographs in the literature^{(13), (14)}.

2.5 Micellar diameter measurement. The hydrodynamic size of surfactant micelles was determined by a submicron particle analyzer (Model 4700 of Malvern Instrument, U.K.). The optical source for the light scattering apparatus was an argon ion laser operating at 488 nm with an output power 5 W maximum (Model Innova 90 of Coherent Co.). Before the measurement, the aqueous solution of a surfactant was passed three times through the membrane filter with $0.1 \mu\text{m}$ in pore size (Cellulose nitrate type of Toyo Roshi Co., Ltd., Tokyo) for optical purification.

3 Results and Discussion

Figure 1 shows the MAC of perfumes as a function of the concentration of DTAC. As the concentration of DTAC increases, MAC of the perfume remains constant up to a certain concentration of DTAC, and then increases rapidly, except for EL. The concentrations where MAC begins to increase correspond to the critical micellar concentration (cmc) of DTAC in the presence of the perfumes^{(15), (16)}. A similar tendency was recognized for other surfactant-perfume systems.

In the case of the solubilization of EL by DTAC solution, the MAC at a low concentration of DATC is somewhat smaller than the solubility of EL in water. Figure 2 shows the phase diagram of DTAC-EL system expressed by the temperature *versus* the ratio of EL concentration to the constant DTAC concentration ($4.0 \times 10^{-2} \text{ M}$). The arrow in the diagram indi-

Fig. 1 The Change in the Maximum Additive Concentration of Perfumes (MAC) as a Function of the Concentration of DTAC at 30°C.

Fig. 2 Phase Diagram of DTAC-EL System. L_1 and LC_1 Describe Micellar and Lamellar Liquid Crystal Phases, Respectively. The arrow corresponds to the MAC determined by turbidity measurement at 30°C.

cates the composition corresponding to the MAC determined by the turbidity measurement at 30°C. It can be postulated from Fig. 2 that the addition of EL to DTAC solutions above MAC yields the phase separation to micellar and lamellar liquid crystal phases, and results in the increment in the turbidity of the solution. In other surfactant-perfume systems, the addition of the perfume above MAC elevates the turbidity of the solution due to the separation of oily droplets from the surfactant solution. Thus, the MAC of EL in DTAC solution estimated by the turbidity method should be regarded as the apparent MAC.

Solubilizing capacity (SC), which is defined as the molar ratio of the solubilized perfume to the micellar surfactant, is an useful parameter to compare the solubilization efficiency of surfactants, because it includes neither the concentration of monomeric surfactant nor the solubility of the perfume in water¹⁷⁾. A larger SC value means that more perfume molecules are solubilized per surfactant molecule in micelles. SC can be estimated from the slope of the plots of MAC against surfactant concentration above cmc. The SC values thus obtained for the present systems are summarized in Table 2, where the value for DTAC-EL system is not included because of its anomalous solubilization behavior as mentioned above. As can be seen in Table 2, SC are always $C_{12}POE_{20} > SDS > DTAC$ for all of the perfumes, except for LN. The order of SC for LN is $C_{12}POE_{20} > DTAC > SDS$.

It has been demonstrated that the perfumes are solubilized into the hydrophilic portion of micelles^{6)~9)}. Thus, some interaction should occur between micellar hydrophilic group region and perfume molecules. Recently, we have investigated the solubilization of 2-phenylethanol and benzyl acetate by sodium dodecyl sulfate and hexadecyl poly(oxyethylene) ether¹⁸⁾, and indicated that the both perfumes are solubilized in the micellar hydrophilic region, and the affinity for the micellar hydrophilic region is enhanced by the increase in the hydrophilicity of the perfume. The result of this investigation suggests that the micellar environment with rather high hydrophilicity is favorable as a solubilization site for perfumes. Thus, it can be postulated that the increment in the hydrophilicity of the micellar hydrophilic portion causes the strong interaction between the hydrophilic portion and perfume molecules, which results

Table 2 Solubilizing Capacity for Perfume at 30°C

Perfume	C ₁₂ POE ₂₀	SDS	DTAC
EL	2.88	1.94	—
LL	1.58	1.34	1.07
BA	0.97	0.58	0.33
IN	0.57	0.44	0.27
HCA	0.17	0.14	0.13
LN	0.44	0.11	0.17

Table 3 Distribution Coefficients of Perfumes between Micelle and Water Phases (K_{mic}) at 30°C.

	$K_{\text{mic}} (\times 10^3)$		
	C ₁₂ POE ₂₀	SDS	DTAC
EL	4.21	3.75	—
LL	4.42	4.13	3.73
BA	1.91	1.43	0.96
IN	35.79	30.12	20.96
HCA	99.92	84.45	79.11
LN	37.02	12.01	17.61

in the large SC value. According to this consideration, the correlation between hydrophilicity of the solubilization site and SC values was examined for the present surfactant perfume systems.

The hydrophilicity of the solubilization site for the perfume can be evaluated by using the distribution coefficient of the perfume between micellar and water phases. The mole fractional distribution coefficients of the perfume compounds between a micellar phase and an aqueous bulk phase (K_{mic}) were estimated by the same method reported in our previous paper^{6),7)}, and are summarized in **Table 3**.

In general, the distribution coefficient of solutes in an organic/water phase is related to that in another organic/water phase by the following relationship^{19)~21)}.

$$\log K_2 = \alpha \times \log K_1 + \beta$$

where K_1 and K_2 are the distribution coefficients of a solute in organic solvent I/water and organic solvent II/water systems, respectively. Both α and β are the experimental parameters characteristic of those solvents. If the value of α is smaller (or larger) than unity, solvent II is more hydrophilic (or less hydrophilic) than solvent I. The α value equal to unity implies that both solvents have the same hydrophilicity¹⁹⁾.

In **Fig. 3**, the K_{mic} in the SDS and DTAC system (K_{SDS} and K_{DTAC}) is plotted as a function of K_{mic} in the C₁₂POE₂₀ system (K_{POE}) on the basis of the above equation, where the result for LN was excluded because of its anomalous solubilizing capacity. The analytical functions and their correlation factors (γ) obtained by the least squares fitting are summarized in **Table 4**. The α value in the relationship between K_{SDS} and K_{POE} is almost equal to unity, whereas the α in the relationship between K_{DTAC} and K_{POE} is somewhat larger than unity. This result indicates that the hydrophilicity is in the following order: C₁₂POE₂₀ $\cong$ SDS > DTAC. The relation among the micellar hydrophilicity of these surfactant species suggests that the interaction between the micellar hydrophilic region and perfume molecules is weaker for DTAC micelle than for C₁₂POE₂₀ and SDS micelles. The smaller SC value for DTAC micelle compared with other surfactant micelles may be attributed to this weaker micelle-perfume interaction resulting from less hydrophilic property of the hydrophilic region in DTAC micelle.

The result for the hydrophilic property of the solubilization site shows that C₁₂POE₂₀ interacts with the perfume similarly to SDS. If the SC of surfactants is determined exclusively by the strength of the interaction between the micellar hydrophilic region and perfume molecules, then we can predict that the values of SC in these surfactant systems become almost equal. However, contrary to this prediction, C₁₂POE₂₀ has a larger value of SC than SDS as shown in **Table 2**.

In addition to the micelle-perfume interaction, the value of SC is also strictly influenced by micellar structures^{17),22)}, because MAC of the perfume depends on the capacity of the mi-

Fig. 3 Distribution Coefficient of Perfumes between Micellar and Water Bulk Phases in the SDS and DTAC Solution (K_{SDS} and K_{DTAC}) *vs.* Distribution Coefficient of Perfumes between Micellar and Water Bulk Phases in the $\text{C}_{12}\text{POE}_{20}$ (K_{POE}) at 30°C.
 —■ SDS *vs.* $\text{C}_{12}\text{POE}_{20}$
 ----● DTAC *vs.* $\text{C}_{12}\text{POE}_{20}$

Table 4 Analytical Functions with Characteristics Parameters (α and β) and Correlation Factor (γ) of Linear Relationship for $\log K_{\text{SDS}}$ and $\log K_{\text{DTAC}}$ *vs.* $\log K_{\text{POE}}$.

$\log K_2 = \alpha \times \log K_1 + \beta$	γ
$\log K_{\text{SDS}} = 1.01 \times \log K_{\text{POE}} - 0.096$	0.955
$\log K_{\text{DTAC}} = 1.05 \times \log K_{\text{POE}} - 0.38$	0.945

celles to accommodate the perfume molecules. **Figure 4** illustrates the micellar diameter obtained over a wide range of surfactant concentrations. As can be seen in **Fig. 4**, the diameter of the micelles decreases in the order $\text{C}_{12}\text{POE}_{20} > \text{DTAC} > \text{SDS}$ at a given surfactant concentration. It can be postulated that, since the surfactants used have the same alkyl chain length, the difference in the micellar diameter is mainly attributed to the difference in the volume of hydrophilic portion of the micelles. According to this interpretation, the hydrophilic portion in the $\text{C}_{12}\text{POE}_{20}$ micelle is considered to be much larger than those in SDS micelle. For this reason, the perfume molecules can be solubilized more greatly in the $\text{C}_{12}\text{POE}_{20}$ micelle, and the SC of $\text{C}_{12}\text{POE}_{20}$ exhibits the largest value as shown in **Table 2**.

The order of SC for LN differs from that for other perfumes, being in $\text{C}_{12}\text{POE}_{20} > \text{DTAC} > \text{SDS}$. This is just the same order as that of the volume of the hydrophilic portion in the micelle, as mentioned above. Due to the extremely low hydrophilicity of LN (see HLB in **Table 1**), the interaction between LN and micellar hydrophilic region should be quite weak. It is

Fig. 4 The Relationship between Micellar Diameter and the Concentration of Surfactants at 30°C.

suggested, therefore, that the capacity of the solubilization site in micelles becomes a dominant factor to determine the SC for LN.

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日本油化学会誌本号掲載 論文要旨

[総説] 合成糖脂質—加水分解酵素モデルとして

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アミノ酸基の結合した環式糖および鎖式糖残基を含む合成糖脂質は、加水分解活性を有し、加水分解酵素モデルとなる。この合成糖脂質モデルを他の多くの提案されている長鎖アルキル基置換アミノ酸型モデルと比較し、その特徴を明らかにしている。すなわち合成糖脂質は、それ自体がミセル・ベシクルを形成する両親媒性物質であるが故に他の多くのモデルと違って両親媒性物質を共存させなくても良いこと、エステル結合ばかりでなく、従来のモデルでは加水分解し得ないアミド結合やグリコシド結合も加水分解できること、また基質識別に関してはアミノ酸のD、L-識別のほかにアミノ酸の種類の識別、グリコシド結合の α 型と β 型の識別も行い得ることなどの特徴を有することが説明されている。その他、合成糖脂質の加水分解の活性点やその活性に及ぼす反応場の影響についても議論されている。

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[報文] イオン系および非イオン系界面活性剤
による合成香料の可溶化徳岡 由一^{※1, ※3}・内山 浩孝^{※1, ※4}・阿部 正彦^{※1, ※2}

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イオン系界面活性剤であるドデシル硫酸ナトリウム(SDS)および塩化ドデシルトリメチルアンモニウム(DTAC)、さらに非イオン系界面活性剤であるポリオキシエチレンドデシルエーテル(C_{12} POE₂₀)による合成香料(オイゲール, リナロール, 酢酸ベンジル, α -ヨノン, α -ヘキシルシンナミックアルデヒドおよびd-リモネン)の可溶化能を測定したところ、d-リモネンを除いたすべての香料の可溶化能は C_{12} POE₂₀ > SDS > DTACであった。またd-リモネンの可溶化能は C_{12} POE₂₀ > DTAC > SDSであった。これらは、界面活性剤-香料間相互作用とミセル中における香料の可溶化領域の大きさのバランスによるものと考えられる。

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[報文] 界面活性剤の光分解 (第18報) 酸化チタンを使用した界面活性剤の無機化におけるT O C測定

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陰イオン系(DBS), 陽イオン系(CTAB, BTDAC, C_{12} -PC), 非イオン系(C_{12} E₅, N-DHA)および両性系(C_{12} -betaine, C_{12} -amidobetaine, C_{12} -HAA)各界面活性剤が紫外線照射下, 半導体光触媒分散系中で光