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ORIGINAL CONTRIBUTION

Influence of synthetic perfumes on stability of O/W emulsion in sodium dodecyl sulfate–*n*-dodecane–water ternary systems

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Abstract Influence of synthetic perfumes having diverse chemical structures such as eugenol, linalool, benzyl acetate, α-ionone, α-hexylcinnamaldehyde, and *d*-limonene on stability of oil-in-water (O/W) emulsion composed of sodium dodecyl sulfate, *n*-dodecane, and water is investigated. Turbidity measurements of the O/W emulsion indicate that the emulsion is stabilized by adding the synthetic perfume, except for *d*-limonene, and that this tendency is remarkable in adding eugenol. The addition of the perfume, especially eugenol, shrinks oil droplets in the O/W emulsion, which inhibits coagulation and/or creaming of oil droplets. When adding eugenol, moreover, ζ-potential of oil droplets increases negatively, and viscosity of the external water phase of the emulsion rises drastically. The increment in ζ-potential and viscosity by the addition of eugenol also prevents oil droplets from coagulation and/or creaming and makes the O/W emulsion still more stable.

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Keywords Synthetic perfume · O/W emulsion · Stability of emulsion · Oil droplet size · ζ-potential · Viscosity of external water phase

Introduction

Synthetic perfumes have been employed in many industrial products such as cosmetics, foods, detergents, pesticides, and coating materials. Synthetic perfumes are then used in various forms with other materials, depending on properties of mediums, solubility of perfumes, stability of perfumes, etc. [1–4].

In particular industrial fields of cosmetic and food sciences, oily synthetic perfumes are mixed with surfactants to produce stable and homogenous oil-in-water (O/W) emulsion. The emulsification makes heat resistance of synthetic perfumes high and constantly releases fragrance from the product [5, 6]. Hence, understanding emulsification of synthetic perfumes by surfactants is essential for their industrial applications.

Stability is one of the most critical factors for consumer product emulsions. A number of papers were then published on emulsion stability in surfactant–perfume systems [7–9]. Pickthall found that hydroxylcitronellal and α-terpineol as a sample of synthetic perfumes destabilized O/W emulsion [10]. Zhang et al. [11] demonstrated that stability of O/W emulsion including phenethyl alcohol, benzaldehyde, or (*S*)–(–)–limonene was dependent on formation of liquid crystal phases in external water phases.

Characteristic fragrance of synthetic perfumes originates in their chemical structures, especially functional groups [12, 13]. Hence, synthetic perfumes are generally classified based on their functional groups into phenols, alcohols, esters, ketones, aldehydes, ethers, hydrocarbons, etc. The previous studies mentioned before paid no attention to the classification of synthetic perfumes, and few studies have examined influence of synthetic perfumes possessing various functional groups on stability of O/W emulsion.

In the present study, we use synthetic perfumes having diverse chemical structures: eugenol (EL) for phenols, linalool (LL) for alcohols, benzyl acetate (BA) for esters, α-ionone (IN) for ketones, α-hexylcinnamaldehyde (HCA) for aldehydes, and *d*-limonene (LN) for hydrocarbons, and we prepare O/W emulsion in sodium dodecyl sulfate (SDS)–n-dodecane–water ternary systems including various concentrations of the synthetic perfume. We then determine the stability of the O/W emulsion and discuss influence of the synthetic perfume on the stability of the O/W emulsion physicochemically.

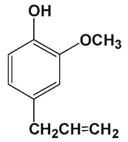
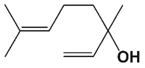
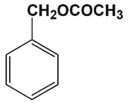
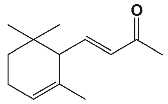
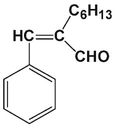
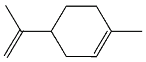
Experimental

Materials

Synthetic perfumes were purchased from Wako Pure Chemical Industries, Ltd. and were used without further purification. Their chemical structure, abbreviation, molecular weight, density, inorganic–organic value (I/O), and purity are listed in Table 1. We used the perfumes having quite diverse chemical structures: EL for phenols, LL for alcohols, BA for esters, IN for ketones, HCA for aldehydes, and LN for hydrocarbons. Their molecular weight and density are almost the same. I/O is a useful index for evaluating hydrophilic–lipophilic balance (HLB) of substances; hydrophilicity of a substance increases with an increase in its I/O [14, 15]. Table 1 then indicates that the hydrophilicity of the perfume used in this study increases in the following order: LN < HCA < IN < BA < LL < EL.

SDS (>95%) and *n*-dodecane (>99%) purchased from Wako Pure Chemical Industries, Ltd. were employed as an emulsifier and an oil phase, respectively. In cosmetic and food sciences, nonionic surfactants are mostly employed as an emulsifier. HLB of nonionic surfactants is markedly affected by additives: inorganic salts and organic compounds. We previously found that cloudy points of nonionic surfactants decreased with an increase in concentration of the perfumes used in this study, which means that HLB of the nonionic surfactant is suppressed by the addition of the perfume [16]. Because the effect of change in HLB of surfactants on stability of O/W emulsion is neglected, we therefore used an anionic surfactant, SDS, as an emulsifier in this study.

Table 1 Chemical structure, abbreviation, molecular weight, density, I/O, and purity of perfume used in this study

Perfume	Chemical structure	Abbreviation	Molecular weight	Density at 30 °C (g/cm^3)	I/O	Purity (%)
Eugenol		EL	164.21	1.06	0.69	> 95
Linalool		LL	154.25	0.85	0.52	> 98
Benzyl acetate		BA	150.17	1.05	0.42	> 98
α-Ionone		IN	192.30	0.92	0.30	> 95
α-Hexcylcinnamaldehyde		HCA	216.33	0.95	0.27	> 97
d-Limonene		LN	136.24	0.84	0.07	> 95

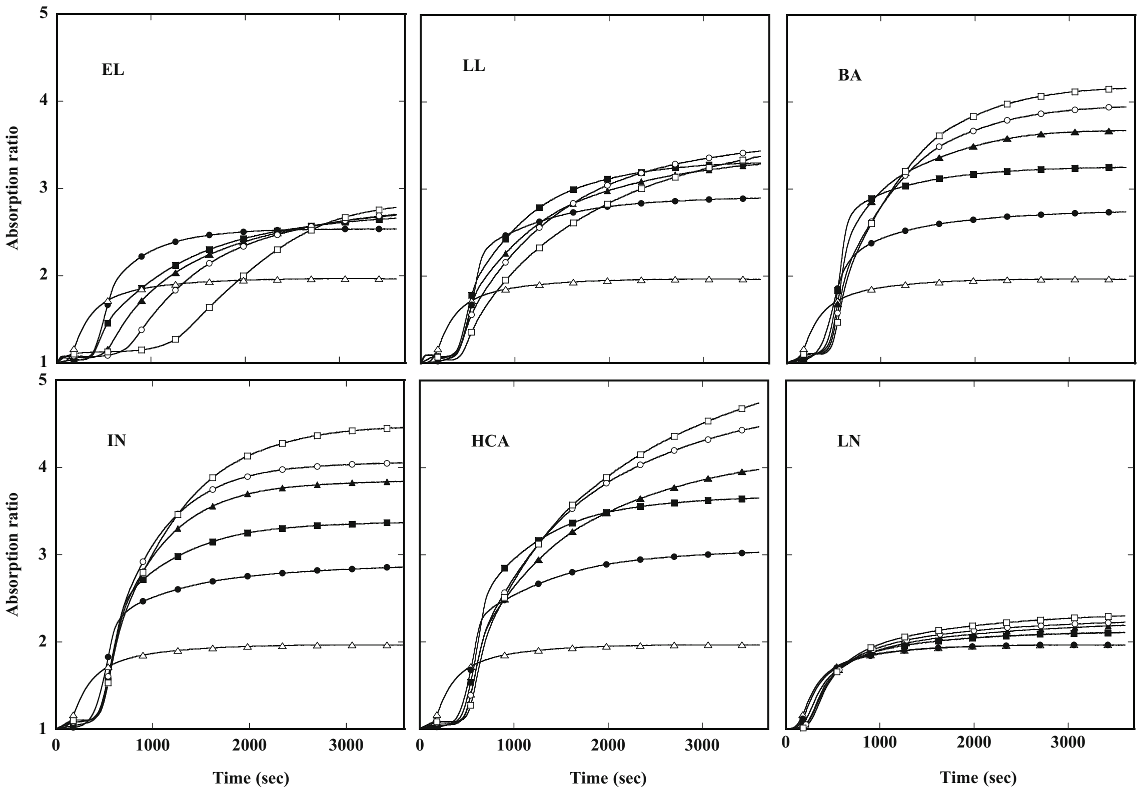


Fig. 1 Time-dependent changes in absorbance ratio at 700 nm of O/W emulsion including various concentrations of synthetic perfumes at 30 °C. *Filled circle*, 0.33 mol/l; *filled square*, 0.67 mol/l; *filled triangle*, 1.0 mol/l; *empty circle*, 1.3 mol/l; *empty square*, 1.7 mol/l; *empty triangle*, without synthetic perfume

Water used in this study was distilled water of which the electric conductivity was less than 5.0 μS/m.

Stability of O/W emulsion

Appearance of emulsion is related to its turbidity. Increase in turbidity of emulsion with progress time is attributable to coagulation, creaming, and resultant coalescence of its dispersed phase [17]. A time-dependent change in turbidity of emulsion is then quite useful to examine emulsion stability.

In this study, turbidity of O/W emulsion was determined by its absorbance at 700 nm. Because no material used absorbed light at 700 nm, the absorbance came from the turbidity of the emulsion. A 0.21-mol/l (6 wt.%) aqueous SDS solution and a perfume-*n*-dodecane mixed solution (perfume concentration of 0.33, 0.67, 1.0, 1.3, and 1.7 mol/l) were prepared. The aqueous SDS and the perfume-*n*-dodecane solutions were mixed at 4:1 in volume ratio, and the mixture was stood for an hour at 30 °C, agitated again with a vortex mixer for 2 min to give homogenous O/W emulsion. Time-dependent changes in 700-nm absorbance of the O/W emulsion were measured with an ultraviolet–visible spectrophotometer (V-550, JASCO Co.) [18, 19]. The measurement was carried out at 30 °C.

Microscopy observation of O/W emulsion

The homogeneous O/W emulsion prepared by the same method in "Stability of O/W emulsion" was observed by a light microscope (ECLIPS ETE300, Nikon Co.) at 30 °C. Moreover, diameters of oil droplets in the O/W emulsion were directly measured from the microscopy observation.

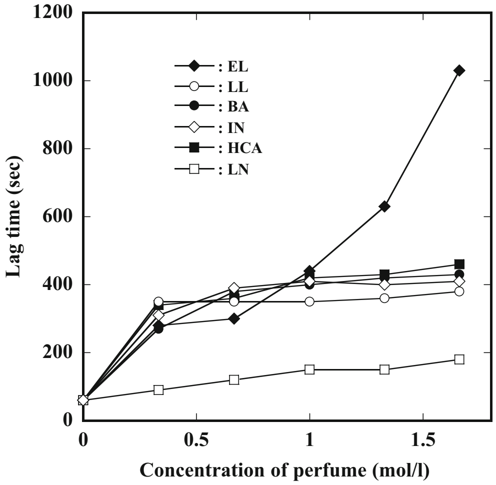


Fig. 2 Changes in lag time of O/W emulsion with perfume concentrations at 30 °C

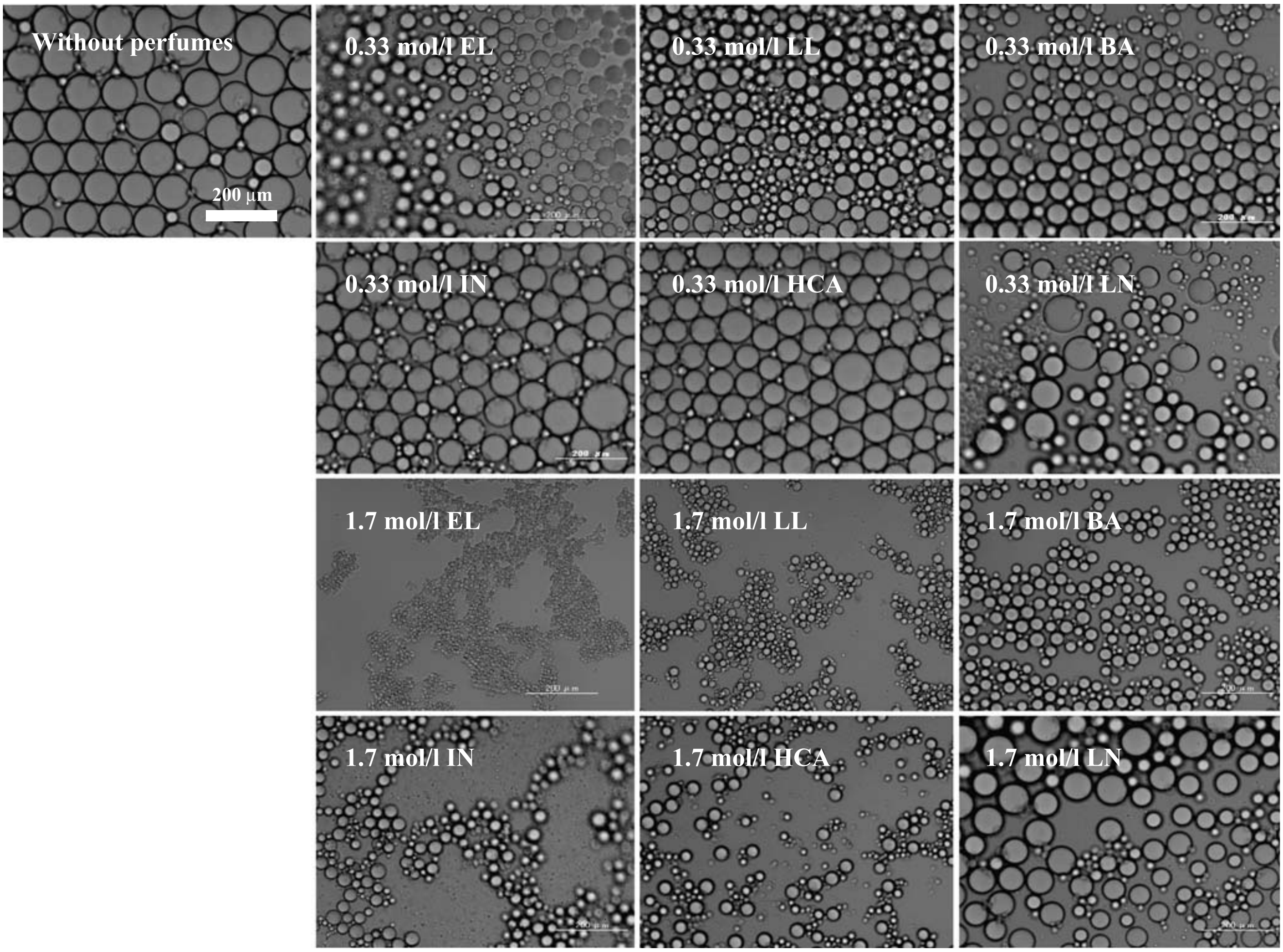


Fig. 3 Microscopy observation of O/W emulsion with 0.33 and 1.7 mol/l of synthetic perfumes at 30 °C

Interfacial tension between perfume-*n*-dodecane mixed solution and water phases

The perfume-*n*-dodecane mixed solution prepared in "Stability of O/W emulsion" was gently poured onto distilled water at 5:1 in volume ratio. It was stood over an hour at 30 °C to provide equilibrium interfaces between the perfume-*n*-dodecane mixed solution and water phases. The interfacial tension was determined by a Du Nouy tensiometer (Taihei Rika Co., Ltd.) at 30 °C.

ζ-potential of O/W emulsion

The aqueous SDS and the perfume-*n*-dodecane mixed solutions prepared in "Stability of O/W emulsion" were mixed at 80:1 in volume ratio, and the mixture was stood for an hour at 30 °C. After then, the mixture was agitated again with a vortex mixer for 2 min to give homogenous O/W emulsion. ζ-potential of the O/W emulsion was determined by a Doppler electrophoretic light-scattering analyzer (Coulter DELSA440, Beckman Coulter, Inc.) at 30 °C.

Viscosity of external water phase in O/W emulsion

The homogeneous O/W emulsion prepared by the same method in "Stability of O/W emulsion" was stood for 24 h

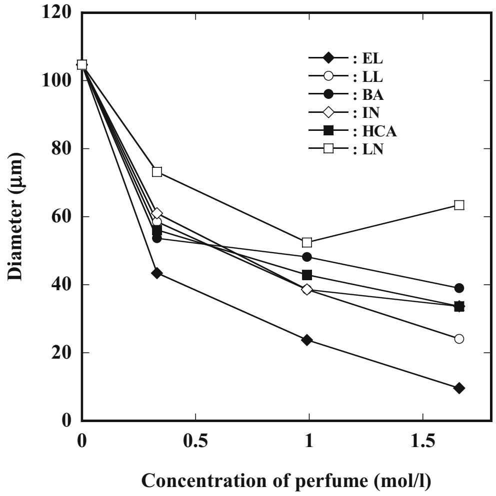


Fig. 4 Changes in O/W emulsion diameters estimated from microscopy observation with perfume concentrations at 30 °C

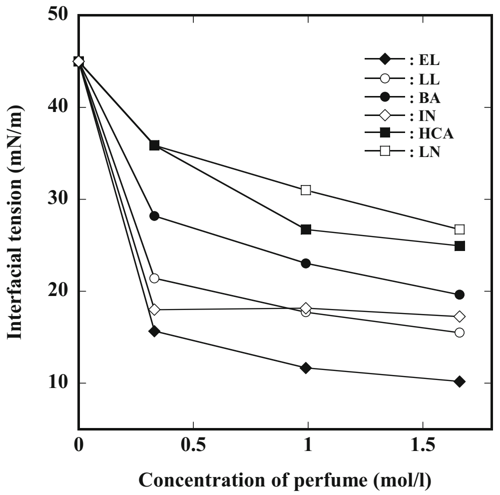


Fig. 5 Changes in interfacial tension between perfume-*n*-dodecane mixed solution and water phases with perfume concentrations at 30 °C

at 30 °C and was separated into an oil and water phase. The water phase was taken out, and its viscosity was measured using a capillary viscometer at 30 °C.

Diameter of molecular aggregate in external water phase of O/W emulsion

The water phase separated from the homogeneous O/W emulsion in "ζ-potential of O/W emulsion" was taken out, and the diameter of molecular aggregates in the water phase was measured by a dynamic light scattering (NICOMP 380ZLS, Particle Sizing Systems Co.) at 30 °C.

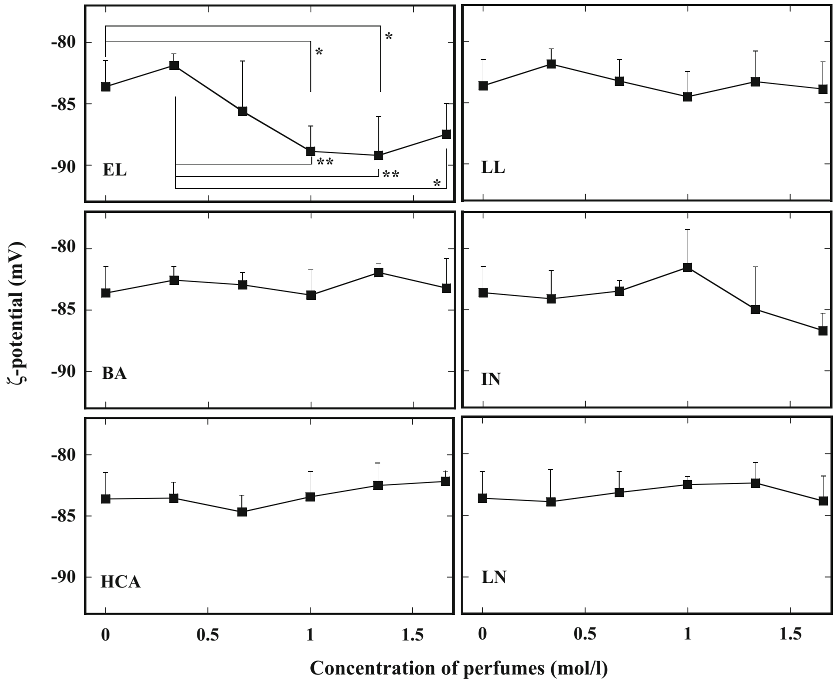
Results and discussion

Figure 1 shows changes in absorbance ratio at 700 nm of O/W emulsion including various concentrations of synthetic perfumes with progress time after agitating the emulsion by the vortex mixer. The absorbance ratio corresponds to the ratio of the 700-nm absorbance at a progress time against that of the initial stage. As the progress time increases, the absorbance ratio is almost constant and increases drastically at a certain progress time.

The increase in absorbance ratio is caused by an increase in turbidity of the emulsion due to coagulation and creaming of oil droplets. The progress time at the beginning of the increase in absorbance ratio is then a valuable index for evaluating emulsion stability. Here, we define the progress time as a lag time. Emulsion having a longer lag time is more stable.

Changes in lag time estimated from Fig. 1 with perfume concentrations are represented in Fig. 2. In the O/W emulsion without the synthetic perfume, the oil phase of which consists of *n*-dodecane alone, the lag time is about 60 s. The addition of the synthetic perfume excluding LN enlarges the lag time. In particular, the lag time considerably increases with an increase in EL concentration and eventually reaches about 17 times as long as the lag time of the emulsion without the synthetic perfume. When adding LN, however, we observe little change in lag time. As a result, we consider that the O/W emulsion is stabilized by adding the synthetic perfume, except for LN, and that this tendency is remarkable in adding EL.

Fig. 6 Changes in ζ-potential of oil droplets in O/W emulsion with perfume concentrations at 30 °C. Values of ζ-potential are mean±S.D. for three determinations. Statistical analysis was performed by ANOVA, followed by Fisher PLSD: *one asterisk*, $p<0.05$, *two asterisks*, $p<0.01$



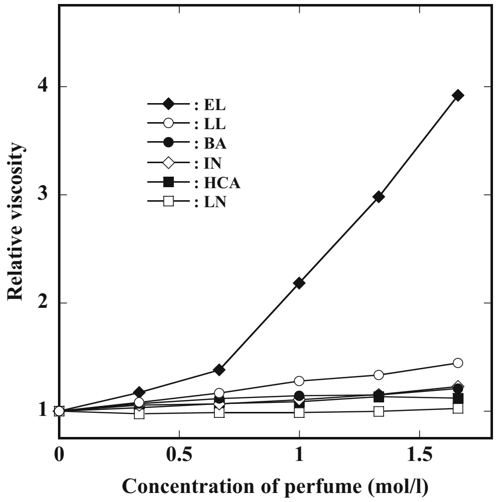


Fig. 7 Changes in relative viscosity of external water phase in O/W emulsion with perfume concentrations at 30 °C

Figure 3 refers to microscopy observation of O/W emulsion with and without the synthetic perfume. We observe the O/W emulsion stood for 3 min after the agitation with the vortex mixer. The magnification of each photograph is the same (×200). We observe numerous oil droplets having different sizes. The diameter of the O/W emulsion without the synthetic perfume is about 100 μm. The addition of 0.33 mol/l of the synthetic perfume slightly reduces the emulsion diameter. Moreover, the addition of 1.7 mol/l of the synthetic perfume, except for LN, makes the diameter still smaller. Noting the change in emulsion diameter with EL concentration, we can comprehend that the emulsion diameter decreases very remarkably and reaches about 10 μm by the addition of 1.7-mol/l EL. These phenomena are also recognized from Fig. 4 that depicts the change in emulsion diameter with the concentration of each synthetic perfume.

Coagulation and resultant coalescence of oil droplets in O/W emulsion cause less stability of the emulsion. In general, coagulation is induced by van der Waals attraction between oil droplets. Moreover, van der Waals attraction between oil droplets, F, is closely related to the oil droplet size, defined as the following equation [20, 21]:

$$F = -\frac{Hr}{12h},$$

where H is Hamaker constant, and r and h are the radius of oil droplets and the interparticle distance between oil droplets, respectively. This equation indicates that van der Waals attraction is proportional to the radius of oil droplets. Decreasing oil droplet size then enhances emulsion stability. In comparing the emulsion stability (Figs. 1 and 2) and the oil droplet size (Figs. 3 and 4), we consider that the addition of the synthetic perfume excluding LN shrinks oil droplets and weakens van der Waals attraction between them, leading to inhibition of coagulation of oil droplets in the O/W emulsion, especially EL.

We previously studied solubilization sites of synthetic perfumes in surfactant micellar systems [16, 19]. We found that the synthetic perfume was located in the hydrophilic portion of the micelle and was transferred from the near hydrocarbon core (palisade layer region) to micellar surfaces as the hydrophilicity of the perfume increased. As can be seen from the I/O value in Table 1, as being the most hydrophilic among the perfumes, EL molecules may be easy to be orientated with SDS molecules on interfaces between oil droplet and external water phases and to reduce the interfacial tension, resulting in the decrease in oil droplet size. On the other hand, because the most hydrophobic perfume LN is hardly oriented on the interface, the interfacial tension and the oil droplet size is unaffected by LN. In fact, when we measure interfacial tension between perfume-n-dodecane mixed solution and water phases shown in Fig. 5, the interfacial tension decreases with increasing perfume concentrations. At the same perfume concentration, in addition, the interfacial tension almost decreases with increasing perfume hydrophilicity.

The orientation of EL on oil droplets in the O/W emulsion affects not only the interfacial tension but also ζ-potential of oil droplets. Figure 6 represents changes in ζ-potential of oil droplets in the O/W emulsion with perfume concentrations. The ζ-potential of the original O/W emulsion without the synthetic perfume is −83 mV. When adding the synthetic perfume into the O/W emulsion, except for EL, we find little change in ζ-potential. However, the ζ-potential significantly decreases to around −90 mV with increasing EL concentration. We can realize from Table 1 that EL belongs to the group of phenols and that proton is weakly

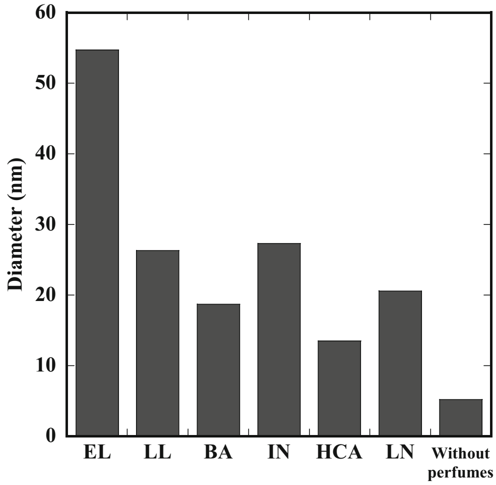


Fig. 8 Molecular aggregate diameters in external water phase of O/W emulsion with 1.7 mol/l of synthetic perfumes at 30 °C

dissociated from its hydroxy group to form phenoxide anion. This weak electrolytic dissociation of EL makes the ζ-potential of oil droplets larger negatively, which also inhibits coagulation between oil droplets.

Creaming rates of oil droplets in O/W emulsion also play an important role in stabilizing the emulsion. In general, reduction in creaming rates facilitates stability of the emulsion [22]. According to Stokes' equation, shown below, creaming rates, V_s, are correlated to the radius of oil droplets, r, the density difference between the oil and external water phases, $\Delta\rho$, and the viscosity of the external water phase, η [22, 23],

$$V_s = \frac{2r^2 \Delta\rho g}{9\eta}.$$

Here, g is the gravitational acceleration. In order to reduce creaming rates, it should be necessary to decrease in the density difference and the radius of oil droplets, and/or to increase in viscosity of the external water phase.

Table 1 indicates that the density of the synthetic perfume is almost the same. Besides supporting that no interaction acts between perfume and *n*-dodecane molecules, we can estimate the density of *n*-dodecane including 1.7 mol/l of the perfume at about 0.8 g/ml (the maximum density is 0.83 g/ml for EL-*n*-dodecane solution and the minimum density 0.77 g/ml for LN-*n*-dodecane solution). Hence, the effect of the density difference on the creaming rate is negligible in each emulsion system.

In consideration of the fact that the diameter of oil droplets decreases with increasing synthetic perfume concentrations, shown in Fig. 4, the creaming rate is suppressed by the addition of the perfume, except for LN. In particular, the marked reduction in emulsion diameter by the addition of EL considerably contributes to the decreasing creaming rate.

Figure 7 depicts changes in viscosity of external water phases of the O/W emulsion with synthetic perfume concentrations. The vertical axis corresponds to relative viscosity of the viscosity of the external water phase against that of the aqueous SDS solution used in the O/W emulsion preparation. The relative viscosity is almost constant despite adding the synthetic perfume, except for EL. On the contrary, the addition of EL drastically enlarges the viscosity. Hence, we also consider that the increasing viscosity of the external water phase by the addition of EL greatly reduces the creaming rate of oil droplets.

SDS molecular aggregates coexist in the external water phase of the O/W emulsion. Diameters of the molecular aggregate in the O/W emulsion with 1.7 mol/l of the synthetic perfume are shown in Fig. 8. The aggregate without the synthetic perfume is about 4 nm in diameter. This diameter originates from SDS micelles solubilizing *n*-dodecane. The addition of 1.7 mol/l of the synthetic perfume into the emulsion makes the diameter larger than 4 nm. In particular, EL expands the aggregate to around 50 nm in diameter, which is twice and/or thrice larger than the diameter of the aggregate with any other perfume. The most hydrophilic perfume EL is likely to act as a co-surfactant and to form microemulsion with SDS molecules in the external water phase. Therefore, the marked enlargement in diameter of SDS molecular aggregates by the addition of EL raises the viscosity of the external water phase, as shown in Fig. 7.

Summary

The O/W emulsion composed of SDS, *n*-dodecane, and water is stabilized by adding the synthetic perfume, except for LN, because the addition of the synthetic perfume shrinks oil droplets in the O/W emulsion and prevents their coagulation and/or creaming. In particular, because of remarkably shrinking oil droplets, EL is superior to any other perfume in stabilizing the O/W emulsion. Moreover, the addition of EL enlarges the ζ-potential of oil droplets negatively and elevates the viscosity of the external water phase in the emulsion, which makes the O/W emulsion still more stable.

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