

Research Article

Stability of O/W Emulsion with Synthetic Perfumes Oxidized by Singlet Oxygen

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We prepared O/W emulsion composed of a synthetic perfume, *n*-dodecane, protoporphyrin IX disodium salt (PpIX-2Na), sodium dodecyl sulfate, and water and investigated oxidative decomposition of the synthetic perfume in the emulsion and change in the stability of the emulsion by singlet oxygen ($^1\text{O}_2$) generated by photosensitization of PpIX-2Na. We used eugenol, linalool, benzyl acetate, α -ionone, α -hexylcinnamaldehyde, and *d*-limonene as a synthetic perfume. The stability of the O/W emulsion including eugenol and linalool significantly decreased with increasing light irradiation time. The decrease in the emulsion stability may be attributable to oxidative decomposition of eugenol and linalool by $^1\text{O}_2$ and enlargement of the oil droplet size.

1. Introduction

Photosensitizing dyes, that is, rose bengal, methylene blue, phthalocyanine, and so on, excited by light convert the energy to oxygen molecules, leading to the formation of singlet oxygen ($^1\text{O}_2$), which is one of the activated oxygen species [1, 2]. When using these dyes in industrial fields, we have been confronted with the degradation of coexisting substances by $^1\text{O}_2$.

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, and so forth [3–5]. In industrial fields of cosmetic and food sciences, moreover, oily synthetic perfumes are mixed with surfactants to produce stable and homogenous O/W emulsion. The emulsification makes the heat resistance of synthetic perfumes high and constantly releases fragrance from the product [6, 7]. So that, many studies on emulsified perfumes have been undertaken [8–12].

We previously investigated the influence of synthetic perfumes on the stability of O/W emulsion composed of

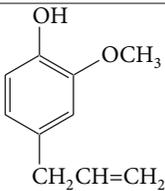
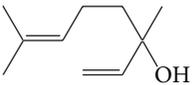
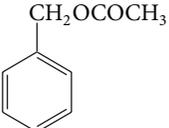
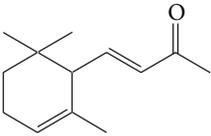
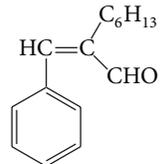
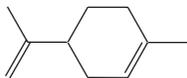
sodium dodecyl sulfate, *n*-dodecane, and water [13]. As a result, shrinking oil droplets in the O/W emulsion, the synthetic perfume prevented the oil droplet from coagulation and creaming, which makes the O/W emulsion still more stable.

In the present study, we prepared O/W emulsion composed of a synthetic perfume, *n*-dodecane, sodium dodecyl sulfate, water, and protoporphyrin IX disodium salt as a photosensitizing dye and investigated oxidative decomposition of the synthetic perfume in the O/W emulsion and change in the stability of the emulsion by $^1\text{O}_2$ generated by the photosensitization of protoporphyrin IX disodium.

2. Experimental

2.1. Materials. We purchased synthetic perfumes, eugenol, linalool, benzyl acetate, α -ionone, α -hexylcinnamaldehyde, and *d*-limonene from Wako Pure Chemical Industries, Ltd. Their chemical structure, abbreviation, molecular weight, density, inorganic/organic value (I/O), and purity are listed in Table 1. We used the perfume having diverse chemical structures: EL for phenols, LL for alcohols, BA for esters, IN

TABLE I: Perfumes used in this study.

Perfume	Chemical structure	Abbreviation	Molecular weight	I/O	Purity (%)
Eugenol		EL	164.21	0.69	>95
Linalool		LL	154.25	0.52	>98
Benzyl acetate		BA	150.17	0.42	>98
α -Ionone		IN	192.30	0.30	>95
α -Hexylcinnamaldehyde		HCA	216.33	0.27	>97
<i>d</i> -Limonene		LN	136.24	0.07	>95

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 hydrophilicity/lipophilicity balance 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 increases as the following order: LN < HCA < IN < BA < LL < EL.

Sodium dodecyl sulfate (SDS, >95%) and *n*-dodecane (>99%), which were purchased from Wako Pure Chemical Industries, Ltd., were employed as an emulsifier and an oil phase, respectively. We also got protoporphyrin IX disodium salt (PpIX-2Na, >95%) from Aldrich Co. We used distilled water of which the electric conductivity was less than 1.0 $\mu\text{S/m}$.

All the materials were used without further purification.

2.2. Preparation of O/W Emulsion including Synthetic Perfumes and PpIX-2Na. We prepared a perfume-*n*-dodecane mixed solution of which the perfume concentration was 1.66 mol/L and an aqueous SDS solution at a concentration of 0.27 mol/L including 1.0×10^{-4} mol/L of PpIX-2Na. The perfume and the SDS solutions were mixed at 1 : 40 in volume ratio, and the mixture was agitated with a vortex mixer to give homogenous O/W emulsion.

2.3. Stability of O/W Emulsion. Appearance of emulsion is related to its turbidity. Change in the turbidity of emulsion with progress time is attributable to coagulation, creaming, and resultant coalescence of its dispersed phase [16]. A time-dependent change in turbidity of emulsion is then useful to examine emulsion stability.

In this study, the turbidity of the O/W emulsion was determined by its absorbance at 700 nm. Since no material used absorbed the light at 700 nm, the absorbance came from the turbidity of the emulsion. With being mixed vigorously, the O/W emulsion was irradiated with light emitted from a metal-halide lamp produced by USHIO Co. for a given time. Figure 1 shows a spectral output of the metal-halide lamp. After the agitation of the light-irradiated O/W emulsion for 2 minutes by a vortex mixer, a time-dependent change in 700 nm absorbance of the O/W emulsion was measured with a UV-VIS spectrophotometer (V-550, JASCO Co.) [17]. The measurement was carried out at 30°C.

2.4. Diameter of Oil Droplets in O/W Emulsion. The O/W emulsion before and after the light irradiation was observed by a light microscope (ECLIPS ETE300, Nikon Co.) at 30°C, and the diameter of oil droplets in the O/W emulsion was directly measured from the microscopy observation.

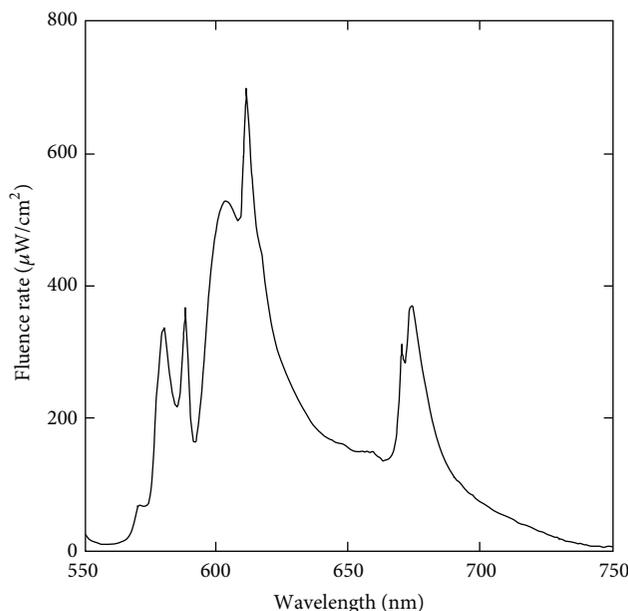


FIGURE 1: Spectral output from metal-halide lamp used.

2.5. Concentration of Synthetic Perfumes before and after Light Irradiation. After the light irradiation, the O/W emulsion was dissolved into ethanol at a volume ratio of 1:6. In addition, we prepared a perfume solution at a concentration of 1.66 mol/L with *n*-dodecane and 5×10^{-5} mol/L PpIX-2Na solution with water-ethanol mixed solvent. We mixed the perfume and the PpIX-2Na solutions at a volume ratio of 1:40, irradiating the mixture with the light from the metal-halide lamp. Thereafter, the perfume concentrations in the O/W emulsion and in the perfume and PpIX-2Na mixed solution were detected by high-performance liquid chromatography (HPLC) coupled to ultraviolet absorbance detection at 200 nm (L-7420, HITACHI Co., Ltd.). The column used was a reverse phase C-18 column ($4.6 \times 150 \text{ mm}^2$, $5 \mu\text{m}$ particle size). The eluate used was a water-ethanol mixed solution at a volume ratio of 1:6, and its flow rate was 1.0 mL/min. The measurement was carried out at 30°C .

3. Results and Discussion

Figure 2 shows time-dependent changes in absorbance at 700 nm of the O/W emulsion irradiated with the light for 0 (○), 30 (●), and 60 (■) minutes. Here, the vertical axis is a ratio of the absorbance at a progress time to that at the beginning (at the progress time of 0). As the progress time increases, the absorbance reduces exponentially in any system. In the case of EL and LL, in addition, the reduction in absorbance is significantly facilitated by an increase in light irradiation time.

The reduction in absorbance is caused by a decrease in turbidity of the emulsion because of coagulation and creaming of oil droplets. The reduction rate of absorbance is then a valuable index for evaluating emulsion stability; that

is, emulsion having a smaller reduction rate is more stable. Changes in reduction rate at the beginning estimated from Figure 2 are represented in Figure 3. Here, the vertical axis depicts a ratio of the reduction rates with the light irradiation to that without the light irradiation. In the case of O/W emulsion with BA (■), IN(□), HCA (◆), and LN (◇), the reduction rate is almost constant despite the light irradiation. Besides, there is a little change in the reduction rate of the O/W emulsion without perfumes (×). In the case of O/W emulsion with EL (●) and LL (○), on the other hand, the reduction rate increases significantly with increasing light irradiation. These findings confirm that the light irradiation depresses the stability of the O/W emulsion including EL and LL.

The light irradiation excites PpIX-2Na and generates $^1\text{O}_2$ through its photosensitization. $^1\text{O}_2$ is one of activated oxygen species and undergoes oxidation reactions. The most well-known $^1\text{O}_2$ -mediated reactions are (1) the ene reaction [18–20], (2) the [2 + 2] cycloaddition [21], and (3) the [4 + 2] cycloaddition [21], as shown in Scheme 1. As can be seen in Table 1, moreover, the synthetic perfume has a C=C bond. We then suggest that the synthetic perfume is easily oxidized by $^1\text{O}_2$.

Figure 4 exhibits the concentration of the synthetic perfume in the O/W emulsion after the light irradiation. The vertical axis is a relative value of synthetic perfume concentrations after and before the light irradiation; when the concentration of the synthetic perfume after the light irradiation is less than that before the light irradiation, a relative value is below unity. Figure 4 indicates that the concentration of the synthetic perfume in the O/W emulsion decreases with an increase in light irradiation time, especially EL and LL. Moreover, Figure 5 expresses HPLC chromatograms of EL and LL in the O/W emulsion before and after the 60-minute

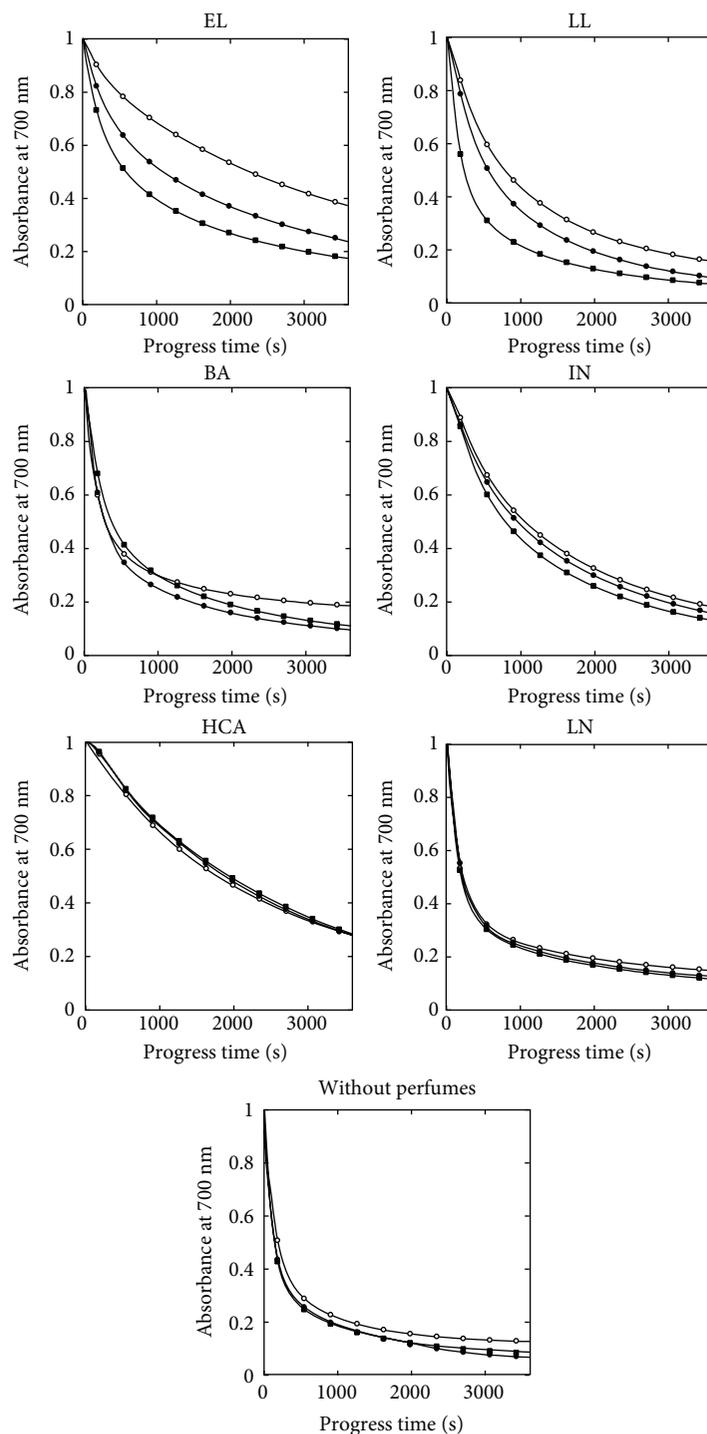


FIGURE 2: Time-dependent changes in absorbance at 700 nm of O/W emulsion after 0-, 30-, and 60-minute light irradiation. Open circle (○), closed circle (●), and closed square (■) correspond to the absorbance change after 0-, 30-, and 60-minute light irradiation, respectively.

light irradiation. In both perfume systems, we can find that the original peak of the synthetic perfume decreases and that a novel peak appears at a shorter retention time after the 60-minute light irradiation. Hence, Figures 4 and 5 reveal that EL and LL are readily decomposed by $^1\text{O}_2$ into more hydrophilic substances.

Next, we discuss why the oxidation decomposition of EL and LL causes the destabilization of the O/W emulsion with them. Since chemical structures of synthetic perfumes are complicated, various kinds of factors of the synthetic perfume affect the stability of emulsion. Zhang et al. reported that the stability of the emulsion with the perfume was

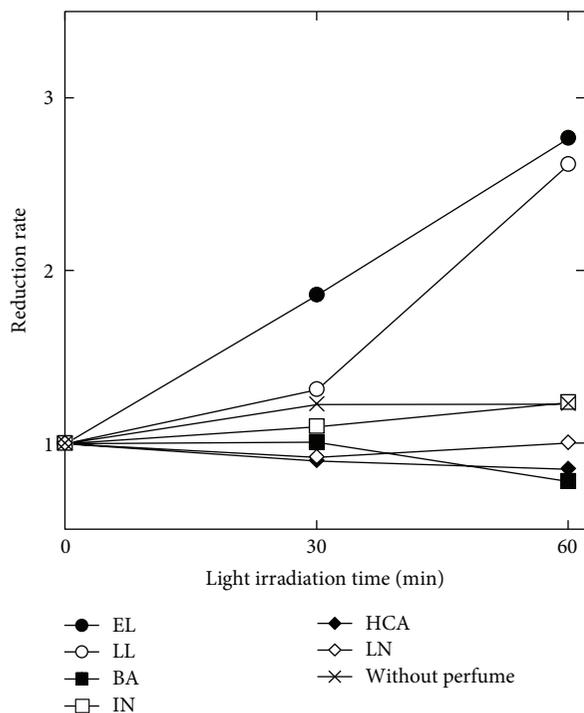


FIGURE 3: Change in the reduction rate of absorbance at 700 nm of O/W emulsion with light irradiation time.

dependent on the density of the oil phase and on the phase changes taking place with changing the surfactant-perfume ratio [10]. Moreover, we previously investigated the influence of synthetic perfumes on the stability of O/W emulsion [13]. As a result, the perfume used in this study, except for LN, shrank oil droplets in the O/W emulsion, resulting in the enhancement of the emulsion stability. Here, we focus on the change in the size of the oil droplet in the O/W emulsion with the oxidation decomposition of the perfume.

In general, coagulation and resultant coalescence of oil droplets in O/W emulsion 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 [22, 23]:

$$F = -\frac{Hr}{12h}, \quad (1)$$

where H is Hamaker constant, and r and h are the radius of oil droplets and the interparticle distance between oil droplets. This equation indicates that van der Waals attraction is proportional to the radius of oil droplets. Decreasing oil droplet size then enhances emulsion stability.

Figure 6 indicates the oil droplet size before and after the 60-minute light irradiation to the O/W emulsion. As can be seen from Figure 6, the size of the oil droplet with EL and LL after the light irradiation is almost twice that before the light irradiation. This means that the light irradiation strengthens van der Waals attraction between oil droplets, leading to

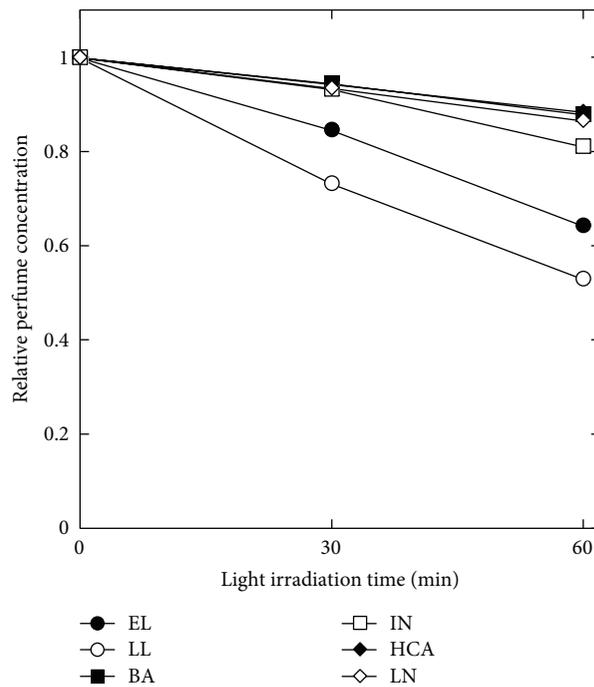


FIGURE 4: Concentration of synthetic perfumes in O/W emulsion after light irradiation.

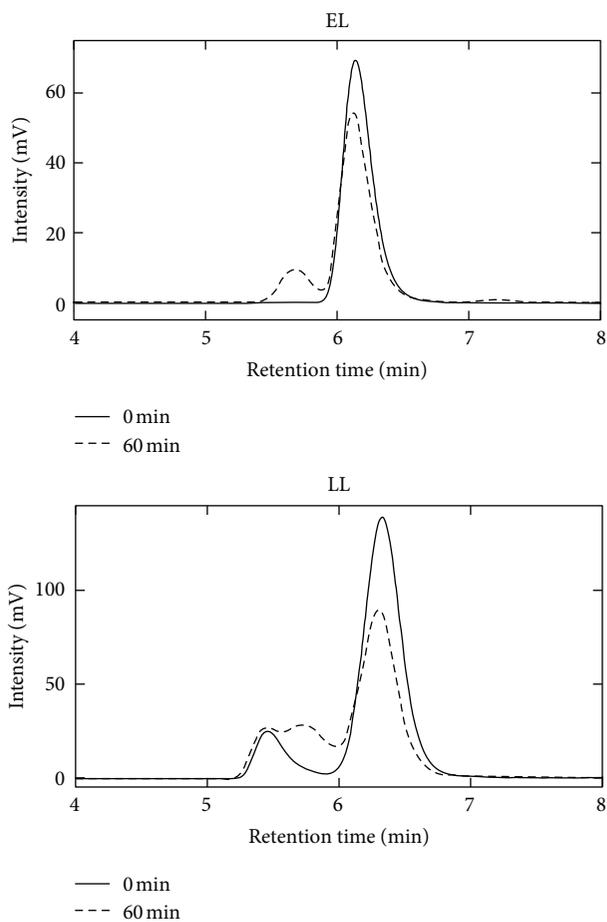


FIGURE 5: HPLC chromatograms of EL and LL in O/W emulsion before and after 60-minute light irradiation.

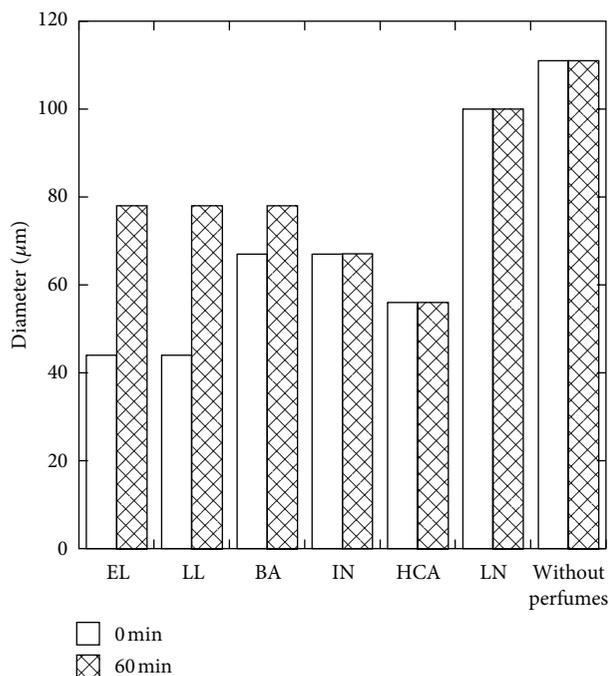


FIGURE 6: Diameter of oil droplets in O/W emulsion before and after 60-minute light irradiation.

the enhancement of the coagulation of oil droplets in the O/W emulsion with EL and LL, as shown in Figure 3. Since the enlargement in the oil droplet size for BA is smaller than that for EL and LL, moreover, there is little influence of the oil droplet size on the stability of O/W emulsion with BA.

We can, therefore, consider from these results that the enlargement in the size of the oil droplet plays a role in the lower stability of the O/W emulsion with EL and LL decomposed oxidatively by $^1\text{O}_2$.

Figure 7 shows the concentration of the synthetic perfume dissolved with PpIX-2Na into the water-ethanol mixed solvent after the light irradiation, as well as Figure 4. The change in perfume concentration with the light irradiation time can be observed in the case of EL, LL, and LN, but not in the case of BA, IN, and HCA; EL, LL, and LN concentrations decrease drastically with increasing light irradiation time. As compared with Figure 4, which depicts the change in perfume concentration with the light irradiation time in the O/W emulsion, it can be found that EL and LL are oxidized by $^1\text{O}_2$ in both the O/W emulsion and the solution systems, and that LN is oxidized in the solution system, but not in the O/W emulsion system.

PpIX-2Na is enough hydrophilic to be dissolved into water, distributed into the external water phase in the O/W emulsion. In fact, we observed that the water phase was colored into red-brown coming from PpIX-2Na in the O/W emulsion. Hence, when the O/W emulsion is irradiated with the light to the O/W emulsion, $^1\text{O}_2$ is generated in the external water phase. Moreover, EL and LL are so more hydrophilic that they can be orientated with SDS on the

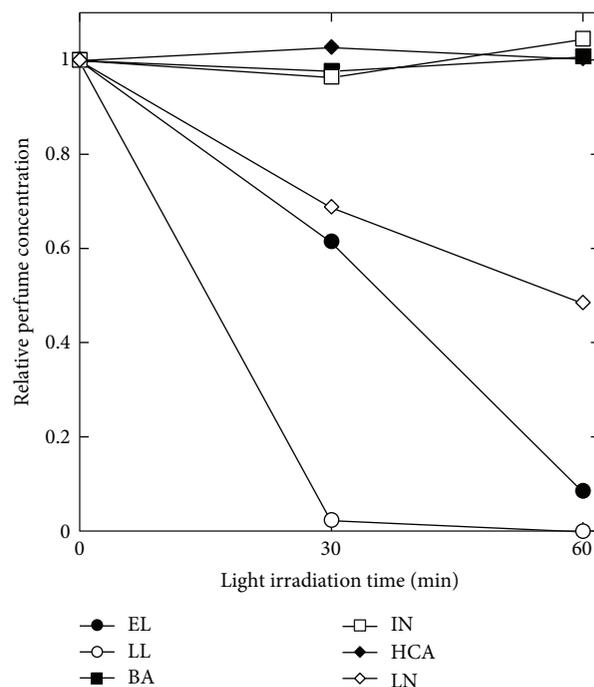


FIGURE 7: Concentration of synthetic perfumes dissolved into water-ethanol mixed solvent after light irradiation.

interface between the oil droplet and the external water phase in the O/W emulsion, like alcohols [24, 25]. On the other hand, BA, IN, HCA, and LN, which are more hydrophobic, are dissolved into the oil droplet in the O/W emulsion.

Consequently, we can consider from these findings that the oxidation decomposition model of the synthetic perfume by $^1\text{O}_2$ in the O/W emulsion is as follows (Figure 8). When irradiated with the light, PpIX-2Na dissolved in the external water phase releases $^1\text{O}_2$ in the water phase. $^1\text{O}_2$ readily attacks EL and LL existing on the interface between the oil droplet and the external water phase. Nevertheless, the reaction of $^1\text{O}_2$ with BA, IN, HCA, and LN is reduced, because these synthetic perfumes are dissolved into the oil droplet in the O/W emulsion. The similar oxidation decomposition model was proposed for the oxidation decomposition of ascorbic acid into O/W microemulsion formed by water, pentanol, and SDS [26].

4. Conclusion

We investigate the change in the stability of O/W emulsion including synthetic perfumes and PpIX-2Na with light irradiation time. The stability of O/W emulsion with EL and LL is depressed after the light irradiation. This may be caused by the oxidation decomposition of EL and LL by $^1\text{O}_2$ generated by the photosensitization of PpIX-2Na and the enlargement of the size of oil droplets in the O/W emulsion.

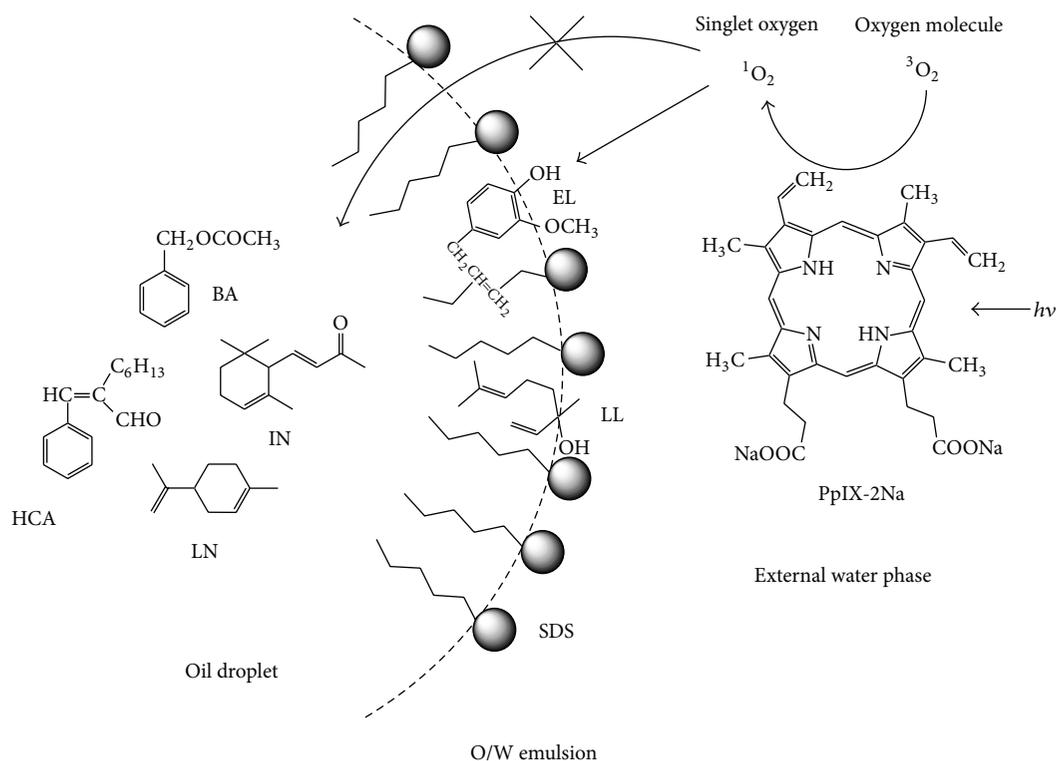
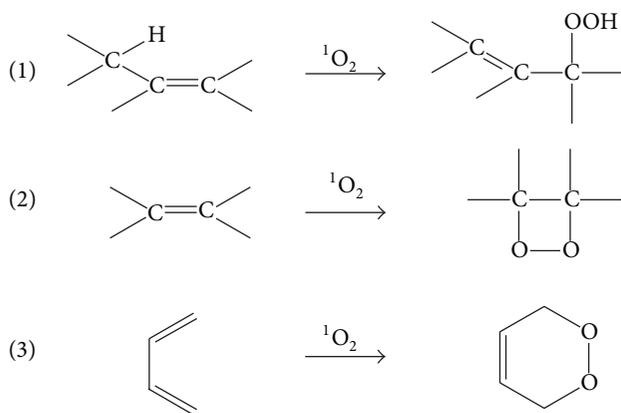


FIGURE 8: Scheme of oxidation decomposition mechanism of synthetic perfumes in O/W emulsion by $^1\text{O}_2$ generated by PpIX-2Na.



SCHEME 1

Acknowledgments

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