# Photocyclodimerization of Cinnamic Acid on a Reaction Matrix: Structural Effect of Molecular Assemblies Constructed by Amphiphilic Compounds

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Light scattering measurement, video-enhanced differential interference microscopic and electron microscopic observations, <sup>1</sup>H-NMR measurement, and photocyclodimerization were carried out for aqueous solutions of alkyldimethylamine oxides ( $C_{12}$ DAO and  $C_{16}$ DAO) and dioctadecyldimethylammonium chloride ( $2C_{18}$ DAC) with addition of cinnamic acid. Molecular assemblies in  $C_n DAO$ :cinnamic acid solutions were converted from micelles to vesicles with increasing mixing ratios of cinnamic acid, while  $2C_{18}DAC$  in water always formed vesicles with addition of cinnamic acid. Structural changes of molecular assemblies constructed by amphiphilic compounds were reflected in the reactivity and stereochemical selectivity of photocyclodimerization. It was concluded that the photodimerization proceeded effectively in vesicles rather than in micelles. The dimerization yields increased with mixing ratio and were in the order of syn-HT  $\leq$  syn-HH  $\leq$  anti-HH (where HT and HH represent head-to-tail and head-to-head, respectively). The product selectivity was discussed in relation to the arrangement of cinnamic acid on molecular assemblies.

#### Introduction

It is known that some systems such as liquid crystals, bilayer membranes, micelles, and organized minerals can serve as reaction matrices for phototransformation, which is basic methodology of photochemistry and can be applied to the development of photoscientific molecular devices.<sup>1-2</sup> The stereoselective photocyclodimerizations of olefins, unsaturated aromatic carboxylates, have been investigated in heterogeneous media.<sup>3-6</sup> The photoreaction proceeds effectively in microheterogeneous matrices such as clays in dispersion or molecular self-assemblies in solution. Moreover, the dimerization yields and the sterical selectivity of dimer species may depend on the location of monomeric acids in the reaction matrix. It is suggested that olefins are intercalated in organized systems and that the preorientation of paired molecules in heterogeneous media is indispensable.

Some investigations of photodimerization were carried out in reversed micelles, and only a few works were reported for the reaction in normal micelles. The reaction occurred above critical micelle concentration.7-10 Organized photodimerizations of 2-indenecarboxylate and cinnamate were compared between systems of normal and reversed micelles, respectively, in water and organic solvents, which were constructed by long-chain amphiphilic compounds.<sup>10</sup> The photoreactions in hexadecyltrimethylammonium and dodecylammonium micelles resulted in the predominant formation of anti-head-to-head (anti-HH) dimers among isomeric dimers, while the reactions yielded synhead-to-head (syn-HH) dimers in reversed micelles and were inefficient in homogeneous isotropic solutions.

In this work, aqueous dodecyl- and hexadecyldimethylamine oxide ( $C_{12}DAO$  and  $C_{16}DAO$ ) solutions are mixed with cinnamic acid and investigated by light scattering, video-enhanced differential interference contrast microscopy (VEM), transmission electron microscopy (TEM), and <sup>1</sup>H-NMR. Investigation

is extended to aqueous solutions of dioctadecyldimethylammonium chloride (2C<sub>18</sub>DAO):cinnamic acid in order to compare the effects of double-chain amphiphilic molecules with vesicleconstruction ability and of single-chain molecules with micelleconstruction ability. Photodimerization is examined, and the effective reactivity and the stereochemical selectivity are discussed in relation to the molecular assembly formation, their structures, and the binding of cinnamic acid. Cinnamic acid can make ion pairs with  $C_n DAO$  and  $2C_{18} DAO$ . Then the location and organized orientation of cinnamic acid on the reaction matrices may be expected to be associated with the specific steric structure of the dimers.

## **Experimental Section**

C12DAO and 2C18DAC were purchased from Fluka, Chemie AG, and Tokyo Kasei Co., Ltd., respectively, and used without any purification.  $C_{16}DAO$  is the same sample previously synthesized and used.<sup>11</sup> Cinnamic acid was purchased from Nacalai Tesque, Inc.Aqueous solutions for light scattering were prepared by mixing cinnamic acid with surfactant so as to be at constant surfactant: cinnamic acid mixing ratios and different total concentrations. Aqueous solutions at a total concentration of  $0.2 \times 10^{-2}$  g cm<sup>-3</sup> were used for microscopic observation and <sup>1</sup>H-NMR measurement. For the photoreaction, a constant concentration (5 mM) of cinnamic acid was dissolved in aqueous surfactant solutions with different surfactant concentrations. The pH's of solutions were varied by adding HCl or NaOH.

Light scattering was measured at 25 °C on an Otsuka Electronics DLS-700 light scattering spectrophotometer at 488 nm wavelength of an argon ion laser with a 21 mm  $\phi$  cylindrical cell. Specific refractive index increment measurements were carried out at 25 °C on an Otsuka Electronics RM-102 refractometer with an iodine lamp at 488 nm by using a Bricetype cell. The apparatus was calibrated by a standard sample, aqueous sucrose solution  $(\partial \tilde{n}/\partial c = 0.144 \text{ cm}^3 \text{ g}^{-1} \text{ at } 488 \text{ nm}$ and 25 °C12). Details of measurement and analysis are described elsewhere.13

Freeze-fracture and freeze-etching replica films for TEM observation were prepared on a Balzers BAF-400 freeze-

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etching apparatus as previously reported.<sup>14</sup> A droplet of solution was rapidly vitrified in liquid nitrogen at its freezing point. On the freeze-etching, the fractured specimen was evaporated at  $\sim -100$  °C for 3-5 min before it was shadowed by platinum and deposited by carbon. TEM observation was performed on a Hitachi H-800 electron microscope operated at 100 kV. VEM observation was carried out on a Nicon NTF-2 transmission differential interference contrast optical microscope attached to a video camera and cabled to a real-time digital image processing system. Both microscopes were operated at room temperature.

<sup>1</sup>H-NMR spectra were recorded on a Varian Gemini-200 spectrometer. Solutions for NMR were prepared by using  $D_2O$  (99.75%, Wako Pure Chemical Industries, Ltd.) as a solvent.

Photodimerization was carried out as follows: reaction solutions in Pyrex tubes were gas-replaced by argon for 10 min and irradiated at room temperature for 12 h at >290 nm wavelength by a Merygoround irradiation aparatus equipped with a 300 W medium mercury arc lamp (Eikosya PIH-300). Irradiated solutions were analyzed by HPLC (Shimadzu LC-6A HPLC chromatograph with a Fine sil C18-10 ODS column) with a flow rate of 1.5 cm<sup>3</sup> min<sup>-1</sup> and detected at 225 nm by UV absorption (JASCO UVITEC-100-III). The eluting solvent was ethanol:water:acetic acid (200:300:2).

#### Results

Light scattering was measured for aqueous surfactant:cinnamic acid solutions which were prepared at constant mixing ratios and different total concentrations. The critical micelle concentration (cmc,  $c_0$ ) of aqueous C<sub>12</sub>DAO:cinnamic acid solutions was determined as usual. The cmc's of C<sub>16</sub>DAO: cinnamic acid and 2C<sub>18</sub>DAC:cinnamic acid systems were less than 10<sup>-5</sup> g cm<sup>-3</sup>, extremely lower than the solution concentrations. The reciprocal scattering intensity  $K(c - c_0)/(R_{\theta} - R_{\theta}^{\circ})$ was calculated, and the molecular weight *M* and radius of gyration  $R_G$  were evaluated according to the following equations:

$$K(c - c_0)/(R_\theta - R_\theta^\circ) = (1/M)(1 + R_G^2 q^2/3) + 2B_2(c - c_0)$$
(1)

$$q = 4\pi \tilde{n}_0 \sin(\theta/2)/\lambda \tag{2}$$

where K is the optical constant, c is the total concentration of surfactant and cinnamic acid, and  $R_{\theta}$  and  $R_{\theta}^{\circ}$  are the reduced



Figure 1. Logarithmic molecular weight of molecular assemblies in aqueous surfactant:cinnamic acid solutions (25 °C) as a function of mixing ratio:  $\bullet$ , C<sub>12</sub>DAO:cinnamic acid;  $\blacksquare$ , C<sub>16</sub>DAO:cinnamic acid;  $\diamond$ , 2C<sub>18</sub>DAC:cinnamic acid.

 TABLE 1: Characteristics of Molecular Assemblies in

 Aqueous Surfactant:Cinnamic Acid Solutions (25 °C) at

 Different Mixing Ratios

minina	27/20	10-6 M						
mixing	oru oc,	10 ° M,	_	_				
ratio	$cm^3 g^{-1}$	g mol <sup>-1</sup>	R <sub>G</sub> , nm	$R_{\rm H}$ , nm	Q			
[Cinnamic Acid]/[C <sub>12</sub> DAO]								
0.2	0.167	0.017						
0.4	0.173	0.097						
0.6	0.176	108	182	121	1.50			
0.8	0.173	161	217	137	1.58			
1	0.170	50.0	96.4	101	0.95			
[Cinnamic Acid]/[C <sub>16</sub> DAO]								
0.2	0.167	0.131						
0.4	0.156	7.13	101					
0.6	0.159	18.8 148						
0.8	0.166	24.2	196	396	0.49			
1	0.168	119	288	407	0.71			
[Cinnamic Acid]/[2C18DAC]								
0.2	0.149	97.9	147	297	0.49			
0.4	0.144	54.4	106	284	0.37			
0.6	0.146	129	176	225	0.78			
0.8	0.138	100	147	246	0.60			
1	0.135	66.0	117	236	0.50			

scattering intensities at c and  $c_0$ , respectively, and at scattering angle  $\theta$ . q is the magnitude of the scattering vector,  $B_2$  is the second virial coefficient,  $\tilde{n}_0$  is the refractive index of solvent, and  $\lambda$  is the wavelength of incident light in vacuo. Numerical values of the molecular weight and radius of gyration are listed in Table 1 with those of the refractive index increment.

Dynamic light scattering results were analyzed on the basis of the following equations:

$$\Gamma/q^2 = D_0 (1 + A R_G^2 q^2) [1 + k_D (c - c_0)]$$
(3)

$$D_0 = k_{\rm B} T / 6\pi \eta_0 R_{\rm H} \tag{4}$$

where  $\Gamma$  is the delay constant,  $D_0$  is the total translational diffusion coefficient, A is a constant, and  $k_D$  is the hydrodynamic virial coefficient.  $k_B$  is the Boltzmann constant, T is the absolute temperature,  $\eta_0$  is the viscosity of solvent, and  $R_H$  is the hydrodynamic radius. Then the hydrodynamic radii were evaluated, and their numerical values are listed in Table 1.

Figures 1 and 2 show molecular weights and radii, respectively, as a function of mixing ratio X = [cinnamic acid]/[surfactant]. The molecular weight for an aqueous C<sub>12</sub>DAO solution without cinnamic acid was cited from a reference.<sup>15</sup> The molecular weight of C<sub>12</sub>DAO:cinnamic acid particles at X = 0.2 was very small as well as at X = 0 and corresponded to that of small micelles. Small-angle neutron scattering examina-



Figure 2. Logarithmic radius of gyration (a) and hydrodynamic radius (b) of molecular assemblies in aqueous surfactant:cinnamic acid solutions (25 °C) as a function of mixing ratio:  $\bullet$ , C<sub>12</sub>DAO:cinnamic acid;  $\blacksquare$ , C<sub>16</sub>DAO:cinnamic acid;  $\blacklozenge$ , 2C<sub>18</sub>DAC:cinnamic acid.

tion confirmed that micelles at X = 0 and 0.2 were sphere and prolate ellipsoid, respectively.<sup>15</sup> Molecular weights increased above X = 0.2 and converged to a constant value,  $10^8$  g mol<sup>-1</sup>, above X = 0.6.

It is certified from VEM and TEM observations that C<sub>16</sub>-DAO in water forms lamellar layers.<sup>16,17</sup> However, when cinnamic acid was added at X = 0.2 in a translucent C<sub>16</sub>DAO solution, the solution became transparent and viscous. Since the molecular weight of particles at X = 0.2 was larger than that of spherical micelles, the formation of rodlike micelles was assumed. This was verified by a small-angle neutron scattering experiment.<sup>15</sup> Molecular weights increased with the mixing ratio and reached around 10<sup>8</sup> g mol<sup>-1</sup> at mixing ratios above X = 0.6.

It is known that double-chain surfactant 2C<sub>18</sub>DAC associates into vesicles. Molecular weights of 2C<sub>18</sub>DAC:cinnamic acid particles were already large even at X = 0.2 and independent of the mixing ratio. The values were on the same order as those of C<sub>12</sub>DAO:cinnamic acid and C<sub>16</sub>DAO:cinnamic acid particles at X = 0.6-1. As seen in Table 1,  $\varrho = R_G/R_H$  for 2C<sub>18</sub>DAC: cinnamic acid particles was 0.4-0.8, suggesting the formation of globular or vesicular particles but not of rodlike particles.<sup>18</sup>  $\varrho$  values less than unity were obtained for C<sub>n</sub>DAO:cinnamic acid solutions with high mixing ratios. Those solutions were translucent as well as 2C<sub>18</sub>DAC:cinnamic acid solutions, being not characteristic of micelles.

Electron microscopic photographs were taken for solutions at a total concentration of  $0.2 \times 10^{-2}$  g cm<sup>-3</sup> and are shown in Figures 3–5. Vesicular textures were observed for C<sub>12</sub>DAO: cinnamic acid mixtures at mixing ratios above 0.4. At X =0.4, there were a few vesicles which were small and unilamellar. In solutions at X = 0.6-1, vesicles with multilamellar layers





Figure 3. TEM photographs of molecular assemblies in aqueous  $C_{12}$ -DAO:cinnamic acid solutions (room temperature) with a total concentration of  $0.2 \times 10^{-2}$  g cm<sup>-3</sup> at different mixing ratios: (a) X = 0.4; (b) X = 0.6; (c) X = 1.

coexisted with small vesicles. The TEM texture for a translucent solution of a C<sub>16</sub>DAO:cinnamic acid mixture at X = 0.1 was lamellar layers, as seen in Figure 4a. A similar texture of lamellar layers has already been reported for an aqueous C<sub>16</sub>-DAO solution.<sup>16,17</sup> C<sub>16</sub>DAO:cinnamic acid solutions at X = 0.4-1 displayed vesicular textures on TEM photographs. Multilamellar layers were few at X = 0.4 but increased with mixing ratios above X = 0.4. However, layers were less than those for C<sub>12</sub>DAO:cinnamic acid mixtures. 2C<sub>18</sub>DAC:cinnamic acid mixtures always formed vesicles with less multilamellar layers, independent of the mixing ratio. These results imply that cinnamic acid contributes to the multilamellar layer formation. The contribution is in the order of C<sub>12</sub>DAO > C<sub>16</sub>-DAO > 2C<sub>18</sub>DAC, suggesting the increase in hydrophobic interaction between surfactant molecules in this order.

VEM observation confirmed that molecular assemblies of  $C_n$ -DAO:cinnamic acid and  $2C_{18}$ DAC:cinnamic acid mixtures at X = 1 were vesicles, as illustrated in Figure 6. Sizes of vesicles in VEM photographs were too large in comparison with radii estimated from TEM and light scattering: radii of gyration and hydrodynamic radii were 96–290 and 100–410, respectively,



Figure 4. TEM photographs of molecular assemblies in aqueous  $C_{16}$ DAO:cinnamic acid solutions (room temperature) with a total concentration of  $0.2 \times 10^{-2}$  g cm<sup>-3</sup> at different mixing ratios: (a) X = 0.1; (b) X = 0.4; (c) X = 0.6; (d) X = 0.8; (e) X = 1.

independent of the mixing ratio, as seen in Figure 2. This means that the polydispersity of vesicles, which is large at larger mixing ratios and in the order of  $C_{12}DAO > C_{16}DAO > 2C_{18}DAC$ . Only larger particles are observed by VEM, while one can observe even smaller particles by TEM.

<sup>1</sup>H-NMR spectra for some surfactant:cinnamic acid solutions at  $0.2 \times 10^{-2}$  g cm<sup>-3</sup> are given in Figure 7 and compared with a spectrum of an aqueous cinnamic acid solution without surfactants. Signals of cinnamic acid in mixed solutions shifted to high magnetic field with increasing mixing ratios up to X =0.4 and broadened above X = 0.4. This implys that cinnamic acid molecules are localized in the nonpolar atmosphere, that is, the hydrophobic interior in bilayers of vesicles.<sup>19</sup> Similar behavior was also observed for aqueous C<sub>16</sub>DAO:cinnamic acid solutions. Aqueous 2C<sub>18</sub>DAC:cinnamic acid solutions presented broad NMR signals at whole mixing ratios from 0.2 to 1, being consistent with the existence of vesicles at every mixing.

HPLC analysis of photoreacted solutions exhibited the existence of *cis*-cinnamic acid, *trans*-cinnamic acid, *syn*-HT, *syn*-HH, and *anti*-HH appearing at 6, 9, 11, 16, and 18 min, respectively, as retention times. Yields of each species were calculated from peak areas on the basis of calibration by independently synthesized cinnamate dimers. Results are listed in Table 2, where the conversion ratio and the structure of the estimated molecular assembly are also included. Figure 8 shows dimer yields as a function of the mixing ratio. The dimerization process is drawn in Chart 2. *Cis*-*trans* isomerization of cinnamic acid occurs rapidly at an early stage of the irradiation procedure, and the stationary state is attained within a few



Figure 5. TEM photographs of molecular assemblies in aqueous  $2C_{18}$ -DAC:cinnamic acid solutions (room temperature) with a total concentration of  $0.2 \times 10^{-2}$  g cm<sup>-3</sup> at different mixing ratios: (a) X = 0.2; (b) X = 0.6; (c) X = 1.

decade min, following the steady increase of cyclodimers by further irradiation.



Photoconversion from the *trans*-isomer to the *cis*-isomer and dimers was least effective for C<sub>16</sub>DAO:cinnamic acid mixtures among three kinds of systems. On the other hand, dimer yields for C<sub>n</sub>DAO:cinnamic acid mixtures were too small to be detected at X = 0.2 but drastically increased with the mixing ratio. The dimer formation for 2C<sub>18</sub>DAC:cinnamic acid mixtures was substantial even at X = 0.2 and increased with the mixing ratio. Dimerization was more remarkable in 2C<sub>18</sub>DAC:cinnamic acid solutions than in C<sub>n</sub>DAO:cinnamic acid solutions. In systems examined here, three kinds of stereoisomers, *syn*-HT ( $\alpha$ -trixyllic acid), *syn*-HH ( $\beta$ -truxinic acid), and *anti*-HH ( $\delta$ -truxinic acid), among expected isomers were observed. Dimer yields increased in the order of *syn*-HT < *syn*-HH <

Microscopic observation and photoreaction were carried out for solutions at different pH's, which were prepared by adding HCl or NaOH to aqueous C<sub>n</sub>DAO:cinnamic acid solutions (pH 4.1) at X = 1. Results are given in Figure 6 and Table 3. While the photoreactivity increased with increasing pH, the photodimerization was maximum at pH 4.1 and was not detectable above pH 6.9, where solutions were transparent and fluid and no textures were observed by VEM, suggesting the disappearance of vesicles. As seen in Figure 6, multilamellar vesicles in C<sub>16</sub>DAO:cinnamic acid solutions at pH 4.1 became smaller and unilamellar with lowering pH. While vesicles at pH 4.1 were stable even at 55 °C, those at pH 1.5 changed to O/W emulsions above 35 °C, resulting in W/O/W emulsions at 55 °C.

## Discussion

While  $C_{12}DAO$  molecules associate into spherical micelles in water,  $C_{12}DAO$ :cinnamic acid mixtures form ellipsoidal micelles at the mixing ratio X = 0.2 and vesicles at X = 0.6-1. In solutions at X = 0.4, ellipsoidal micelles may coexist with vesicles because the molecular weight is not large enough to be vesicles but the existence of some vesicles is observed.  $C_{16}DAO$  molecules are organized in lamellar layers in water and at X = 0.1, whereas those form rodlike micelle at X = 0.2

 TABLE 2: Photochemical Yields of Cinnamic Acid and Structures of Molecular Assemblies in Aqueous Surfactant:Cinnamic Acid Solutions (Room Temperature) at Different Mixing Ratios (Unit %)

mixing ratio	conv	cis-isomer	syn-HT	syn-HH	anti-HH	total dimers	molecular assemblies
			ſCi	nnamic Acid]/	[C <sub>12</sub> DAO]		
0.2	80.7	80.7		· · · · · ·			ellipsoidal micelle
0.4	69.5	62.4	3.2		3.9	7.1	ellipsoidal micelle + vesicle
0.6	69.6	52.3	3.7	5.3	8.4	17.3	vesicle
0.8	65.3	36.6	5.6	6.4	16.7	28.7	vesicle
1	64.8	33.0	3.7	11.2	16.9	31.8	vesicle
			ſCi	nnamic Acid]/	[C <sub>16</sub> DAO]		
0.2	45.5	45.5					rodlike micelle
0.4	35.9	31.8			4.1	4.1	vesicle
0.6	22.9	17.5		1.4	4.1	5.4	vesicle
0.8	50.1	20.1	6.2	7.4	16.4	30.0	vesicle
1	47.2	16.1	4.7	8.9	17.5	31.1	vesicle
			ſĊi	namic Acid]/[	2C <sub>18</sub> DACl		
0.2	57.0	36.4		7.2	13.4	20.6	vesicle
0.4	52.7	32.7	0.5	7.1	12.4	20.0	vesicle
0.6	63.7	28.1	6.2	11.5	18.1	35.6	vesicle
0.8	65.3	27.8	9.6	11.2	16.7	37.5	vesicle
1	67.7	28.8	7.9	12.7	18.3	38.9	vesicle





**Figure 7.** <sup>1</sup>H-NMR spectra for aqueous surfactant:cinnamic acid solutions (25 °C) with a total concentration of  $0.2 \times 10^{-2}$  g cm<sup>-3</sup>: (a) cinnamic acid; (b) C<sub>12</sub>DAO:cinnamic acid (X = 0.2); (c) C<sub>12</sub>DAO: cinnamic acid (X = 0.4); (d) C<sub>12</sub>DAO:cinnamic acid (X = 1); (e) C<sub>16</sub>-DAO:cinnamic acid (X = 1); (f) 2C<sub>18</sub>DAC:cinnamic acid (X = 1).

and vesicles at X = 0.4-1. 2C<sub>18</sub>DAC molecules always construct vesicles at whole mixing ratios.

Structures of molecular assemblies may be compared with the photodimerization of cinnamic acid: it is concluded that vesicular bilayer arrangement of surfactants is superior to the micellar one in their photodimerization, as verified from the comparison of the photoreactivity for surfactant:cinnamic acid mixtures at X = 0.2. Cinnamic acid molecules can be oriented more preferably in vesicles than in micelles.

Vesicles constructed at higher mixing ratios have higher dimerization reactivity, since quantity, localization, and orientation of cinnamic acid in vesicles are promoted with increasing mixing ratios and the pairing of cinnamic acids to form dimers increases in probability.

Dimerization in vesicles is more superior for the  $2C_{18}$ DAC: cinnamic acid system than for  $C_n$ DAO:cinnamic acid systems. It can be interpreted that vesicles constructed by a double-chain surfactant are more compact in molecular arrangement on their surface. Growth of multilamellar vesicles and regularity of layers are not always concerned with the photodimerization



[cinnamic acid]/[surfactant]

Figure 8. Photodimerization yield of cinnamic acid in aqueous surfactant:cinnamic acid solutions (room temperature) with cinnamic acid of 5 mM as a function of mixing ratio:  $\oplus$ , C<sub>12</sub>DAO:cinnamic acid;  $\oplus$ , 2C<sub>18</sub>DAO:cinnamic acid.

TABLE 3: Photochemical Yields of Cinnamic Acid in Aqueous Surfactant:Cinnamic Acid Solutions with X = 1(Room Temperature) at Different pH's (Unit %)

pН	conv	cis-isomer	syn-HT	syn-HH	anti-HH	total dimers		
[Cinnamic Acid]/[C <sub>12</sub> DAO]								
1.14	46.3	43.7		2.6	-	2.6		
2.53	37.8	32.2		3.5	2.0	5.6		
3.83	60.4	34.8	3.5	7.2	14.9	25.6		
4.12	64.8	33.0	3.7	11.2	16.9	31.8		
4.88	69.4	49.1		8.0	12.3	20.3		
6.92	79.5	79.5						
11.7	81.5	81.5						
12.9	91.5	91.5						
[Cinnamic Acid]/[C <sub>16</sub> DAO]								
1.13	41.1	27.6		7.8	5.7	13.5		
3.83	48.6	22.1	3.4	7.8	15.2	26.5		
4.10	47.2	16.1	4.7	8.9	17.5	31.1		
4.80	57.8	30.6	4.7	6.8	15.7	27.2		
6.93	72.2	72.2						
12.9	77.1	77.1						

because lamellarities of  $2C_{18}$ DAC:cinnamic acid vesicles are less than those of  $C_n$ DAO:cinnamic acid vesicles. This means that the dimerization is related to only local arrangement of cinnamic acid on vesicular surfaces.

The estimated arrangement of cinnamic acid on bilayers of vesicles is schematically illustrated in Figure 9. It is known that aromatic carboxylic acids can be intercalated into molecular assemblies constructed by surfactants.<sup>19</sup> On the other hand, weak acids such as cinnamic acid form ion pairs with weak base surfactants,  $C_nDAO$ , and a cationic surfactant,  $2C_{18}DAC$ . Then cinnamic acids bind electrostatically with surfactants, and some of them are located on the bilayer surface, while some are intercalated into bilayer by directing aromatic groups toward the interior of the bilayer. Both types of cinnamic acid molecules are oriented antiparallel on bilayers.

If a molecule on the vesicular surface and an intercalated molecule are photodimerized, products are *syn*-HT, where *trans*cinnamic acid molecules bind in manner of head-to-tail direction. When the dimerization occurs between intercalated molecules, head-to-head isomers, *syn*-HH and *anti*-HH, where cinnamic acids arrange in a head-to-head direction, are formed.

At low mixing ratios, molecules on the surface and intercalated molecules may exist with almost equivalent fractions. With increasing mixing ratio, the fraction of intercalated cinnamic acid increases preferably, since the hydrophobicity of cinnamic acids and the interaction between their aromatic rings are high. Therefore, the yields of *syn*-HH and *anti*-HH increase with mixing ratio and HT isomers are formed with less yield than HH isomers.



Figure 9. Schematic illustration for location of cinnamic acid on surfactant vesicles: upper, low mixing ratio; lower, high mixing ratio.

The yield of *anti*-HH is always higher than that of *syn*-HH. This may occur owing to the difference in energetic stabilization. The former is more stable than the latter, the steric strain energy being ca. 2 kcal/mol higher.<sup>20,21</sup> This contributes the formation of *anti*-HH with high yield.

When HCl is added into  $C_n DAO$ :cinnamic acid mixtures, ionized  $C_n DAO$  molecules increase but ionized cinnamic acid molecules decreases. Since the ion-pairing between the surfactant and cinnamic acid decreases, the photodimerization yield decreases. Ionized  $C_n DAO$  molecules act to decrease vesicular size. Moreover, with increasing temperature, the hydrophobicities of nonionic cinnamic acid molecules are promoted, and the solution is separated into cinnamic acid-rich and cinnamic acidpoor phases. Then emulsions which are coated by  $C_n DAO$ monolayers are observed at high temperatures. At higher pH, cinnamic acid molecules are ionized and disperse as free species in water. Then  $C_n DAO$  molecules cannot form vesicles, and the photodimerization does not occur.

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#### **References and Notes**

 (a) Thomas, J. K. The Chemistry of Excitation at Interfaces; ACS Monograph 181; American Chemical Society: Washington, DC, 1984. (b) Fox, M. A. Organic Phototransformations in Non-homogeneous Media; American Chemical Society: Washington DC, 1985. (c) Ramamurthy, V. Tetrahedron 1986, 42, 5753. (d) Kalyanasundaram, K. Photochemistry in Microheterogeneous Systems; Academic Press, Inc.: Orlando, FL, 1987. (e) Takagi, K.; Sawaki, Y. Crit. Rev. Biochem. Mol. Biol. 1993, 28, 323. (2) (a) Cohen, M. D. Angew. Chem., Int. Ed. Engl. 1975, 14, 386. (b) Quina, F. H.; Mobius, D.; Carroll, F. A.; Hopf, F. R.; Whitten, D. G. Z. Phys. Chem. N. F. 1976, 101, 151. (c) Nerbonne, J. M.; Weiss, R. G. J. Am. Chem. Soc. 1978, 100, 2571.

(3) Wolff, T.; Muller, N. J. Photochem. 1983, 22, 61; 1983, 23, 131.

(4) Takagi, K.; Miyake, N.; Nakamura, E.; Usami, H.; Sawaki, Y. J. Chem. Soc., Faraday Trans. 1 1988, 84, 3475.

(5) Ueno, A.; Moriwaki, F.; Iwama, Y.; Suzuki, I.; Osa, T.; Ohta, T.; Nozoe, S. J. Am. Chem. Soc. **1991**, 113, 7034.

(6) Usami, H.; Takagi, K.; Sawaki, Y. J. Chem. Soc., Faraday Trans. 1992, 88, 77.

(7) Takagi, K.; Suddaby, B. R.; Vadas, S. L.; Backer, C. A.; Whitten,
 D. G. J. Am. Chem. Soc. 1986, 108, 7865.

(8) Takagi, K.; Fukaya, H.; Miyake, N.; Sawaki, Y. Chem. Lett. 1988, 1053.

(9) Takagi, K.; Nambara, E.; Usami, H.; Itoh, M.; Sawaki, Y. J. Chem. Soc., Perkin Trans. 1 1991, 655.

(10) Takagi, K.; Itoh, M.; Usami, H.; Imae, T.; Sawaki, Y. J. Chem. Soc., Perkin Trans. 2 1994, 1003.

(11) Hashimoto, K.; Imae, T. Langmuir 1991, 7, 1734.

(12) Halmer M. J. Am. Chem. Soc. 1948, 70, 3985.

- (13) Imae, T.; Ikeda, S. Colloid Polym. Sci. 1987, 265, 1090: Imae, T.
   J. Phys. Chem. 1988, 92, 5721; J. Colloid Interface Sci. 1989, 127, 256.
- (14) Imae, T.; Takahashi, Y.; Muramatsu, H. J. Am. Chem. Soc. 1992, 114, 3414.
- (15) Okamura, H.; Imae, T.; Furusaka, M. J. Colloid Interface Sci. 1994, 168, 217.
  - (16) Imae, T.; Trend, B. J. Colloid Interface Sci. 1991, 145, 207.
  - (17) Imae, T.; Iwamoto, T. J. Colloid Interface Sci. 1991, 152, 289.

(18) Van De Sandre, W.; Persoons, A. J. Phys. Chem. 1985, 89, 404.

- (19) Rao, U. R. K.; Manohar, C.; Valaulikar, B. S.; Iyer, R. M. J. Phys.
- Chem. 1987, 91, 3286.
  - (20) Allinger, N. L. J. Am. Chem. Soc. 1977, 99, 8127.
  - (21) Allinger, A.; Tuh, Y. QCPE 1980, 12, 395.

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