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ORIGINAL CONTRIBUTION

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Self-assembly formation of amphiphilic molecules mixed with photoreactive, aromatic unsaturated-acids: examination by light scattering

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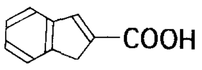
Abstract Light scattering measurement was carried out for aqueous solutions of amphiphilic molecules mixed with aromatic unsaturated carboxylic acids. Their structures are discussed according to sizes of molecular assemblies evaluated. In aqueous solutions of hexadecyltrimethylammonium hydroxide with 2-indenecarboxylic acid, short rodlike micelles were formed on mixing at a ratio of 1:1. Particles in aqueous solutions of dodecyldimethylamine oxide and cinnamic acid varied from micelles to vesicles with increasing cinnamic acid concentration. The structures were related to the effective photocyclodimerization of olefins and the stereochemical selectivity of cyclodimers.

Key words hexadecyltrimethylammonium hydroxide – 2-indenecarboxylic acid – dodecyldimethylamine oxide – cinnamic acid – light scattering – micelle – vesicle – photocyclodimerization

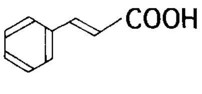
Introduction

Molecular assembly systems are attractive not only in photochemistry but also for practical applications such as photoscientific molecular devices [1, 2]. It is known that photocyclodimerization proceeds effectively in heterogeneous micromatrices rather than in homogeneous solutions [3–6]. Photodimerization of aromatic unsaturated acids was carried out in organized systems such as clays, micelles, vesicles, etc. [7–10]. It has been confirmed that the dimerization yields and the stereoselectivity of cyclodimers change from system to system. In this way, many investigations of photoreaction were focused into the reactivity and the selectivity, but not into the structures of matrices.

In this work, we investigate light scattering of aqueous solutions of amphiphilic molecules mixed with aromatic unsaturated carboxylic acids or olefins. Two kinds of systems, mixtures of hexadecyltrimethylammonium hydroxide ($C_{16}H_{33}N(CH_3)_3OH$, $C_{16}TAOH$) with 2-indenecarboxylic acid (In) and of dodecyldimethylamine oxide ($C_{12}H_{25}N(CH_3)_2O$, $C_{12}DAO$) with cinnamic acid (Cin), are examined, and the sizes and shapes of molecular assemblies are discussed. The structures are related to the effective photoreactivity and the stereochemical selectivity, which have already been reported [10, 11].



2-indenecarboxylic acid (In)



cinnamic acid (Cin)

Experimental section

An equimolar complex of C_{16}TAOH with In was prepared according to a previously reported method [10]. The complex was dissolved in water to prepare solutions with equimolar mixing ratio. Solutions with 1.1 mixing ratio (= [olefin]/[surfactant]) were prepared by adding In to solutions of the equimolar complex. Samples of C_{12}DAO and Cin were purchased from Fluka, Chemie AG and Nacalai Tesque, Inc., respectively, and solutions with different mixing ratio were prepared at different concentrations. While C_{16}TAOH: In complex was less soluble in water (at most ~7 mM for equimolar complex), C_{12}DAO: Cin complex was soluble in water. Water was redistilled from alkaline $KMnO_4$.

Light-scattering measurement was performed on Otsuka Electronics DLS-700 light-scattering spectrophotometer with 488 nm argon ion laser. Cells with 21 and 12 mm diameters were used. Solutions were purified by filtrating them through Millipore membranes or prepared by dust-free solvents. The scattering angle was changed from 20 to 150°. Specific refractive index increments were measured on an Otsuka Electronics RM-102 differential refractometer. Measurement was carried out at 488 nm wavelength with a 50 W iodine lamp by using a Brice type cell. Details of measurement and analysis are described elsewhere [12, 13].

Analysis

Reduced Rayleigh scattering intensity R_θ as a function of scattering angle θ and total concentration c of surfactant and olefin is described as follows [14]:

$$K(c-c_0)/(R_\theta - R_\theta^0) = (1/M)(1 + R_G^2 q^2/3) + 2B_2(c-c_0) \quad (1)$$

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

where K is the optical constant, and c_0 is the critical micelle concentration (CMC). R and R^0 are the reduced scattering intensities at c and c_0, respectively. q is the magnitude of scattering vector, B_2 is the second virial coefficient, $\tilde{n}_0$ is the refractive index of solvent, and λ is the wavelength of incident light in vacuo. Molecular weight M and radius of gyration R_G can be calculated by extrapolating to zero particle concentration and zero scattering angle on the basis of Eq. (1).

Mutual diffusion coefficient evaluated from dynamic light scattering is written as

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

where Γ is the delay constant, D_0 is the total translational diffusion coefficient, A is a constant, and k_D is the hydrodynamic virial coefficient [15, 16]. If particles are a sphere, the hydrodynamic radius (Stokes radius) R_H is related to the total translational diffusion coefficient by a Stokes–Einstein equation:

$$R_H = k_B T/6\pi\eta_0 D_0\,, \quad (4)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity of solvent. Then, the hydrodynamic radius is calculated from double extrapolation to zero particle concentration and zero scattering angle.

Results and discussion

C_{16}TAOH: In complex

Significant angular dependence of light scattering was not observed for aqueous C_{16}TAOH: In solutions. Figure 1 shows reciprocal scattering intensity at 90 degree scattering angle as a function of particle concentration $c - c_0$ for solutions with equimolar mixing ratio at different temperatures. Debye plots decreased initially with concentration and leveled off to constant values at concentrations above 0.2×10^{-2} g cm^{-3}, indicating increase of particle sizes and their constriction. The constant values can be reciprocal molecular weights, since the second virial coefficients are almost null. Numerical values are listed in Table 1 with those of specific refractive index increment $\partial\tilde{n}/\partial c$ and CMC. The CMCs were obtained as the surfactant concentrations where the reduced scattering intensity differences began to increase.

Solutions with 1.1 mixing ratio were also examined at 30 °C, and results are plotted in Fig. 1. Molecular weight

Fig. 1 Debye plots for aqueous C_{16}TAOH: In solutions. Mixing ratio: closed symbols, 1; open symbol, 1.1. ●, 25 °C; ▲, 27.5 °C; ■□, 30 °C.

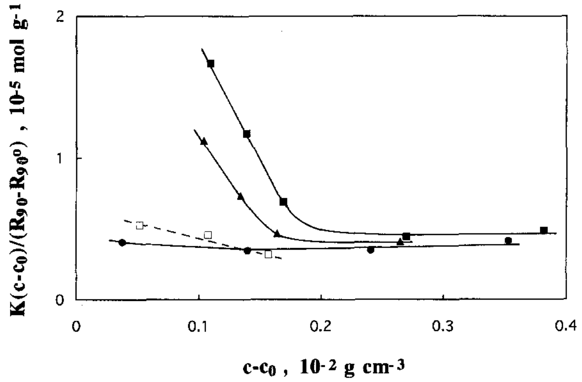


Table 1 Characteristics of molecular assemblies in aqueous C_{16}TAOH: in solutions.

Mixing ratio[a]	T, °C	$\partial \tilde{n}/\partial c$, $cm^3 g^{-1}$	c_0, $10^{-2} g cm^{-3}$	M, 10^5 [b]	m	R_H, nm[b]
0	25					2.3[c]
1	25	0.198	0.059	2.70	609	10.2
	27.5	0.200[d]	0.035	2.44	550	
	30	0.202	0.030	2.17	489	9.2
1.1	30	0.182	0.052	3.16[e]	712[e]	10.9[e]

a) Mixing ratio = [In]/[C_{16}TAOH].
b) Averaged values of data at particle concentrations above 0.2×10^{-2} g cm^{-3}.
c) Cited from Biresaw et al. (1985) [19].
d) Intrapolated.
e) A value at 0.158×10^{-2} g cm^{-3}.

was evaluated from a reciprocal scattering intensity at a concentration of 0.158×10^{-2} g cm^{-3}, above which C_{16}TAOH: In was insoluble. Numerical values of molecular weight and concerning parameters are included in Table 1.

Molecular weights for systems examined here were only $2.2\text{–}3.2 \times 10^5$, but were larger than those of spherical micelles as reported generally. As seen in Table 1, aggregation numbers m of mixed micelles were 490–710, indicating the formation of short rodlike micelles. The formation of rodlike micelles by ionic surfactants with organic counter-ions was reported for alkyltrimethylammonium salicylate [17, 18]. Hexadecyltrimethylammonium salicylate molecules in water are associated into short rodlike micelles with aggregation numbers of 440–880 at 15–35 °C. The aggregation numbers are comparable to those of C_{16}TAOH: In micelles. While sizes of C_{16}TAOH: In micelles decreased with increasing temperature, they increased with increase in mixing ratio of In. Those behaviors are characteristics of ionic micelles.

On dynamic light scattering, mutual diffusion coefficients could be observed at 20 and 30 degree scattering angles and were averaged. Since mutual diffusion coefficients were independent at concentrations above 0.2×10^{-2} g cm^{-3}, those at pertinent concentrations were averaged, and hydrodynamic radii were calculated on the basis of Eqs. (3) and (4). Hydrodynamic virial coefficients were taken to be null. The evaluated values are listed in Table 1, where a value for C_{16}TAOH micelles without In [19] is also included. Hydrodynamic radius of 2.3 nm for C_{16}TAOH micelles corresponds to that of spherical micelles. Then, values of 9.2–10.9 nm for C_{16} TAOH: In micelles confirm the formation of rodlike micelles.

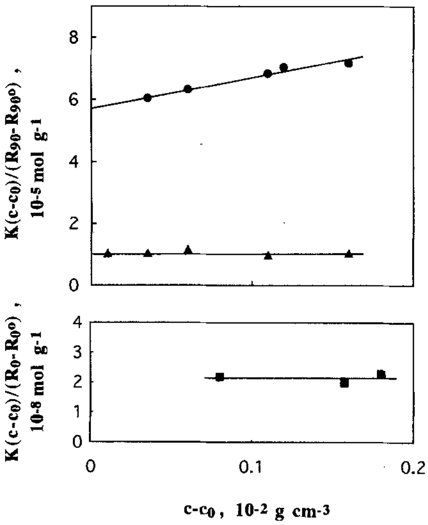


Fig. 2 Debye plots for aqueous C_{12}DAO: Cin solutions at 25 °C. Mixing ratio: ●, 0.2; ▲, 0.4; ■, 1.

C_{12}DAO: Cin Complex

Light scattering for aqueous C_{12}DAO: Cin solutions at 25 °C did not display detectable angular dependence at mixing ratios of 0.2 and 0.4. Debye plots at 90 degrees are given in Fig. 2. Reciprocal scattering intensities increased with particle concentration for solutions at 0.2 mixing ratio, indicating a positive virial coefficient. Then, molecular weights were evaluated from the extrapolation to zero concentration. On the other hand, the reciprocal scattering intensities were independent of the concentration of solutions at 0.4 mixing ratio and revealed negligible contribution of second virial coefficient.

The angular dependence of light scattering was observed for solutions with higher mixing ratio than 0.4. Then, reciprocal scattering intensities were extrapolated to zero scattering angle. Debye plot at 0 degrees for solutions at equimolar mixing ratio showed insignificant contribution of second virial coefficient within examined concentrations, as seen in Fig. 2. Similar results were obtained for solutions at mixing ratios of 0.45–1. Molecular weights were evaluated as averaged values for data obtained at different concentrations. Radii of gyration were calculated from the initial slope of angular dependence of light

Table 2 Characteristics of molecular assemblies in aqueous C_{12}DAO: Cin solutions at 25 °C

Mixing ratio[a]	$\partial\tilde{n}/\partial c$, $cm^3\,g^{-1}$	c_0, $10^{-2}\,g\,cm^{-3}$	M, 10^5[b]	m	R_G, nm[b]	R_H, nm[b]
0[c]		0.059	0.154[d]	67		
0.2	0.167	0.040	0.170[d]	66		
0.4	0.173	0.040	0.971	336		
0.45	0.176[e]	0.033[e]	670	2.3×10^5	121	217
0.5	0.178	0.025	4000	13×10^5	532	343
0.6	0.176[e]	0.024[e]	1100	3.4×10^5	182	121
0.8	0.173[e]	0.023[e]	1600	4.6×10^5	217	137
1	0.170	0.021	500	1.3×10^5	96.4	101

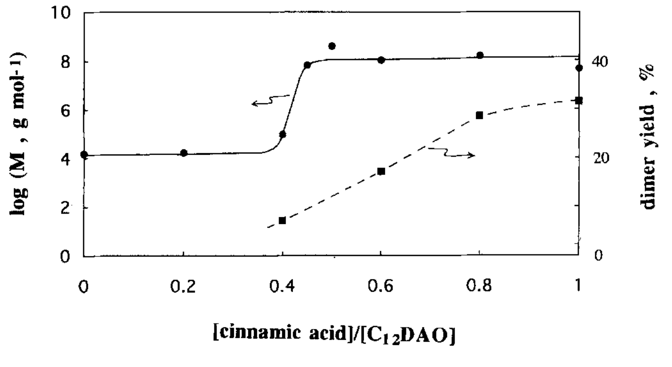
a) Mixing ratio = [Cin]/[C_{12}DAO].
b) Averaged values of data at different particle concentrations.
c) Cited from Ref. [11].
d) Obtained by extrapolating to zero particle concentration.
e) Intrapolated.

scattering. Table 2 lists numerical values of parameters obtained from analysis. For comparison, values for C_{12}DAO micelles without olefins in water [11] are included in Table 2.

Since dynamic light scattering had angular dependence for solutions at mixing ratios above 0.45, mutual diffusion coefficients were extrapolated to zero scattering angle. Mutual diffusion coefficients at zero scattering angle did not display significant concentration dependence at concentrations examined here. Therefore, the averaged values were evaluated, and hydrodynamic radii were calculated according to equations described above. Numerical values are given in Table 2.

Figure 3 shows logarithmic molecular weight of C_{12}DAO: Cin particles as a function of mixing ratio. Molecular weights increased remarkably at mixing ratio between 0.4 and 0.45, and those were almost constant at mixing ratios below 0.4 and above 0.45. Molecular weights at mixing ratios below 0.4 corresponded to those of small micelles, as suggested from aggregation numbers. Detailed analysis of small-angle neutron scattering data showed that micelles at mixing ratios of 1 and 0.2 were spherical and ellipsoidal, respectively [20].

Fig. 3 Logarithmic molecular weights (●) and dimer yields (■) as a function of mixing ratio for aqueous C_{12}DAO: Cin solutions at 25 °C



Molecular weights at mixing ratios above 0.45 were four orders larger than those of small micelles. Numerical values of radius of gyration and hydrodynamic radius also supported the formation of large particles in solutions at mixing ratios of 0.45–1. The valuation of those values is rather complicated, because the coexistence of micelles and vesicles, the polydispersity of vesicles, and the multilamellarity of vesicle bilayers [11] must be considered. Because such solutions were translucent, but not viscous, this suggests that large particles are not rodlike micelles. Angular dependence of static light scattering for such solutions displayed a downward curvature. This kind of curvature is characteristic of globular particles rather than to ellipsoidal or rodlike particles [21, 22]. Vesicular textures were detected on electron microscopic observation for solutions with mixing ratios above 0.4 [11].

Molecular assembly formation and photocyclodimerization

The photocyclodimerization of In in C_{16}TAOH: In complex with equimolar mixing ratio was carried out at room temperature, and the dimer yield of 22% was obtained [10]. Among isomer species, anti-HH isomer (18%) and syn-HH isomer (4%) were preferentially produced rather than others. Short rodlike micelles were formed in the reactive solution.

Spherical micelles are formed in aqueous C_{12}DAO solutions without additives, but C_{12}DAO micelles change their structure under the existence of additives. It was concluded that, when cinnamic acid was added into aqueous C_{12}DAO solutions, molecular weights of particles increased, and vesicles were formed above mixing ratio of 0.45. The more detailed information was obtained from the small-angle neutron scattering measurement and the electron microscopic observation [11]. The formation of ellipsoidal micelles was suggested at 0.2 mixing ratio. Particles at 0.4 mixing ratio were a mixture of ellipsoidal micelles and vesicles.

Dimer yields for photoreaction of Cin in aqueous C_{12}DAO: Cin solutions [11] are plotted in Fig. 3 and compared with molecular weights of particles in solutions. Dimers were detectable at mixing ratio above 0.4. It was concluded that the photodimerization of Cin was more superior on vesicular bilayers than on micelles [11]. Dimer yields increased with increasing mixing ratio. It is indicated that quantity, localization and orientation of Cin in vesicles are promoted with increasing the mixing ratio, and therefore the coupling probability of cinnamic acids in vesicles increases, following the increase in dimerization.

Product distribution of photodimerization for C_{12}DAO: Cin solutions increased in the order of syn-HT < syn-HH < anti-HH [11]. Similar results were also observed for C_{16}TAOH: In solutions. This may be related to the orientation of olefins on particles. Aromatic carboxylic acids such as In and Cin form ion-pairs with C_{16}TAOH and C_{12}DAO. Then, the olefins bind electrostatically near surfaces of particles. Since organic acids can be intercalated into molecular assemblies because of their hydrophobicity, some olefin molecules are inserted into particles by directing an aromatic group toward the interior, while some others are arranged on particle surfaces. If the photocyclodimerization occurs between acids on particles or between intercalated acids, anti-HH and syn-HH dimers are preferentially formed.

Whereas short rodlike micelles were formed in C_{16}TAOH: In solutions at equimolar mixing ratio, particles in C_{12}DAO: Cin mixtures at equimolar mixing were vesicles. This may be due to the difference of the orientation of olefins on particles. The In molecules on C_{16}TAOH particles can preferably bind in the manner of arranging on particle surfaces, but Cin molecules can be predominantly intercalated into C_{12}DAO particles. This results in the different variation of the structure of molecular assemblies from spherical micelles to short rodlike micelles for C_{16}TAOH: In particles and to vesicles for C_{12}DAO: Cin particles.

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