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Stabilization of a Labile cis-Azobenzene Derivative with Amphiphilic Cyclodextrins

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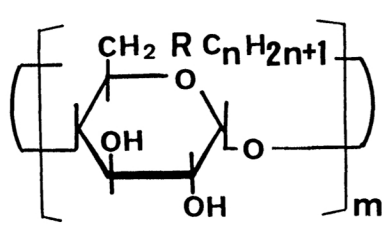
The cis-isomer of p-Methyl Red (**cis-p-MR**) was appreciably stabilized by inclusion in equimolar amphiphilic heptakis(6-alkylamino-6-deoxy)cyclodextrins (C_nN**-CDs**) in either chloroform solution or the Langmuir-Blodgett (LB) films, as compared with that in the isolated state. Amino moieties in the cyclodextrin derivatives were found to be essential for a tight inclusion of **p-MR** and also for the stabilization of cis-isomer.

It is widely known that cyclodextrins (**CDs**) form inclusion complexes with a number of organic molecules without any covalent bonds. **α-CDs** and **ß-CDs**, which are composed of six and seven glucopyranose units respectively, have different internal diameters of the cavity (**α-CDs**:ca.0.5 nm and **ß-CDs**:ca.0.7 nm) for the selective inclusion. These host-guest compounds, therefore, have aroused an increasing interest in wide fields of science and technology.[1)]

Recently, we have reported a new type of photoreactive LB films which is composed of $C_{12}N$**-ßCD** including such azobenzenes without long alkyl chains as **p-MR**, Methyl Orange, and p-(phenylazo)benzoic acid.[2,3)] During the experiments, considerable stabilization for unstable cis-isomers of azobenzenes was observed in



abbreviation

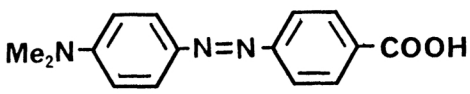
$C_{12}N$**-ßCD** : n=12, m=7, R=NH

$C_{16}N$**-αCD** : n=16, m=6, R=NH

$C_{16}S$**-ßCD** : n=16, m=7, R=S

$C_{12}SO$**-ßCD** : n=12, m=7, R=SO

Amphiphilic cyclodextrins



p-Methyl Red (**p-MR**)

these LB films. Although the cis-isomer of **p-MR** having electron push-pull substituents (dimethylamino and carboxyl groups) was extremely labile in chloroform solution at room temperature, it was significantly stabilized by inclusion in the LB films of C_{12}**N-ßCD.**[3,4] However, not all of **CDs** have exhibited the stabilization effect. It seems to be important for extensive utilizations of **CDs** to reveal the factors which have influence on the stabilization phenomena. This report describes the effects on the stabilization of labile **cis-p-MR** by forming the inclusion complex with **CDs** in LB films and chloroform solution.

The trans-isomer of **p-MR** (**trans-p-MR**) was irradiated with a monochromatic light at its absorption maximum until the photostationary state (PSS) was reached, and then kinetics of thermal cis-to-trans isomerization in the LB films and chloroform solution was investigated by UV-visible spectroscopy. Fast decay of the cis-isomer in solution was measured by a flash photolysis system consisted of a storage scope and a pulsed dye laser (full width at half-maximum : 20 ns).[5] In the case of slow decay, the isomerization was monitored with a spectrophotometer at the absorption maximum of the trans-isomer after its PSS on irradiation with a 500 W super-high pressure xenon lamp through a monochromator.

Figure 1 shows plots of the first order kinetics for thermal cis-to-trans isomerization of the inclusion complexes in solution and the LB films. In the chloroform solution of complexes, the cis-isomers reverted thermally to their trans-isomers by first order processes at room temperature, while deviation from the first-order kinetics was observed in the LB films of C_n**N-CDs.**[3,4] The rate constants and half-lifes for the thermal cis-to-trans isomerization of the inclusion complexes are summarized in Table 1.

Although **trans-p-MR** in C_{16}**N-αCD** was less converted into **cis-p-MR** than in C_{12}**N-ßCD** at PSS, **cis-p-MR** was considerably stabilized in the LB films which is shown in

Table 1. Rate constants and half-lifes of **p-MR** in LB films and $CHCl_3$ at 25 °C

Run	CD	LB or $CHCl_3$[a]	First-order rate constant k / s^{-1}	Half-life $T_{1/2}$
1	none	$CHCl_3$	1.2×10^{2}	6.0 ms
2	C_{12}**N-ßCD**[b]	LB		55 s [c]
3	C_{16}**N-αCD**	LB		68 s [c]
4	C_{12}**N-ßCD**	$CHCl_3$	1.3×10^{-3}	9.1 min
5	C_{16}**N-αCD**	$CHCl_3$	8.7×10^{-4}	13.6 min
6	C_{16}**S-ßCD**	$CHCl_3$	1.1	640 ms
7	C_{12}**SO-ßCD**	$CHCl_3$	4.2	160 ms
8	**TriMe-ßCD**	$CHCl_3$	1.4×10^{2}	4.9 ms
9	**DiMe-ßCD**	$CHCl_3$	94	7.4 ms

a) [**CD**] = [**p-MR**] = 2.5×10^{-5} mol dm^{-3}.

b) Ref. 3.

c) At 20 °C.

Table 1 (Run 2 and 3). Conversions of **trans-p-MR** into the cis-isomer included in C_{16}**N-αCD** and C_{12}**N-βCD** at PSS were estimated to be 8% and 30%, respectively, from the absorbance. It is attributed to difference in the cavity diameters of C_n**N-CDs** and also probably to morphological characteristics of the LB films.

In dilute chloroform solution, the stability of **cis-p-MR** in C_n**N-CDs** (molar ratio **p-MR:**C_n**N-CD** = 1:1, 2.5×10^{-5} mol dm^{-3}) was about 100 000-fold more stable in comparison with that of free **cis-p-MR** (Run 4 and 5). As shown in Fig.2, a hypsochromic shift was observed in the UV-visible spectra of **trans-p-MR** in C_n**N-CDs.** These results indicate specific interactions between **p-MR** and **CDs** having possess hydrophobic cavities, in a non-aqueous solution.[6] Conversions of **trans-p-MR** into **cis-p-MR** in C_{16}**N- CD** and C_{12}**N-βCD** at PSS were estimated to be about 60% in both **CDs.**[7]

On the other hand, an equimolar addition of amphiphilic heptakis(6-hexadecylthio-6-deoxy)-ß-cyclodextrin (C_{16}**S-βCD**) or heptakis(6-dodecylsulfinyl-6-deoxy)-ß-cyclodextrin (C_{12}**SO-βCD**) without amino moieties to the solution had only a slight effect on the stability of **cis-p-MR** (Run 6 and 7). The hypsochromic shift was not observed in these solutions. The inclusion of **p-MR** in LB films was not achieved with C_{16}**S-βCD** and C_{12}**SO-βCD** by the procedure as in the previous papers.[2,8] Furthermore, in the case of equimolar mixtures of **p-MR** and chloroform-soluble methylated **ß-CDs** such as heptakis(2,3,6-tri-O-methyl)-ß-cyclodextrin (**TriMe-βCD**) and heptakis(2,6-di-O-methyl)-ß-cyclodextrin (**DiMe-βCD**), the rate of thermal isomerization resembled to that of isolated **p-MR** in chloroform solution (Run 8 and 9).

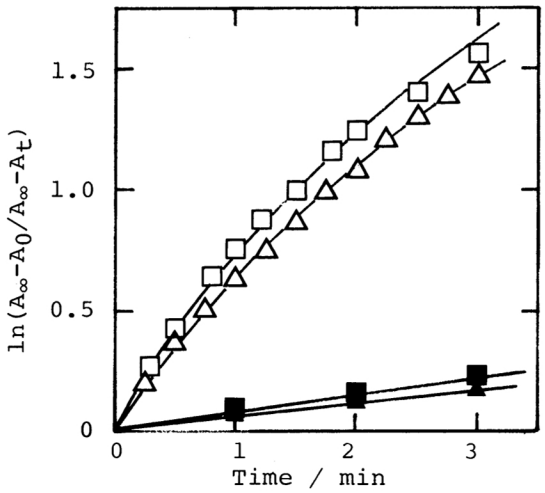


Fig.1. The first order kinetics plots for cis-to-trans thermal isomerization. A_0, A_t, and A_∞: absorbance at initial state, after t and ∞ min, respectively.

□:the LB film of **p-MR** in C_{12}**N-βCD**
△:the LB film of **p-MR** in C_{16}**N-αCD**
■:the solution of **p-MR** in C_{12}**N-βCD**
▲:the solution of **p-MR** in C_{16}**N-αCD**

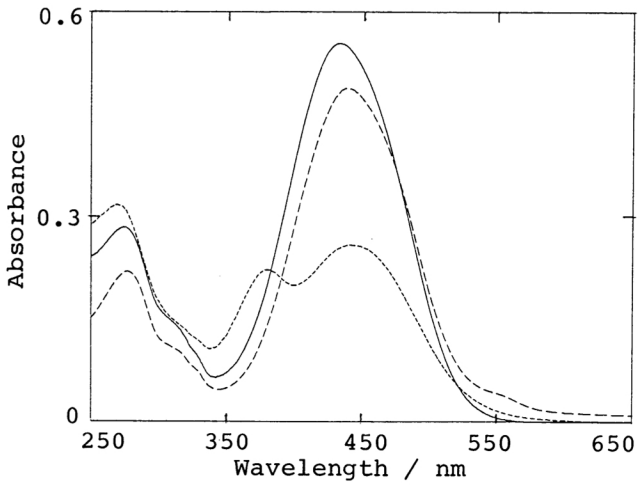


Fig.2. UV-Vis spectra of **p-MR**, and the complex of **p-MR** and C_{12}**N-βCD** (1:1), $CHCl_3$.

(----): **p-MR**
(———):the complex before irradiation
(------):the complex at PSS

Study of inclusion complexes on irradiation has indicated the ejection of the cis-isomer of azobenzenes from non-substitued **ß-CD** in an aqueous solution.[9,10] Our experiments have shown the abilities of **C_nN-CDs** for the inclusion of **p-MR** in chloroform solution and LB films, while the examination of molecular models suggested that the geometry of cis-isomer disfavored a stable complex with **ß-CD.**

In conclusion, the present study has revealed that the amino moiety in **CD** derivatives of **C_nN-CDs** plays an important role for the complexation between **C_nN-CDs** and **p-MR,** and also for the stabilization of **cis-p-MR** in the inclusion complexes, in chloroform solution and LB films. In the case of **C_{16}S-ßCD** and **C_{12}SO-ßCD,** the high rate constants suggest that the complex formation with **p-MR** is weaker than in the case of **C_nN-CDs.** Further investigations on detailed functions of amino groups in **CDs** are now in progress.

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