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Hiroshi Hachisako[a]; Tetsuya Yamazaki[a]; Ryoichi Murakami[a]; Kimiho Yamada[a]
[a] Department of Applied Chemistry, Graduate Course, Kumamoto Institute of Technology, Kumamoto, Japan

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PRELIMINARY COMMUNICATIONS

Planarity recognition of cationic dyes by anionic, crystalline bilayer aggregates

by HIROSHI HACHISAKO*, TETSUYA YAMAZAKI,
RYOICHI MURAKAMI and KIMIHO YAMADA
Department of Applied Chemistry, Graduate Course,
Kumamoto Institute of Technology, 4-22-1 Ikeda,
Kumamoto 860, Japan

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Steric selectivity in terms of molecular planarity of cationic dyes was investigated using anionic bilayer aggregates. Planar cationic dye (*para*-type stilbazolium) could be incorporated into the hydrophobic region of anionic crystalline bilayer aggregates, whereas structurally related, less planar dyes (*ortho*-type stilbazolium) could not be incorporated in spite of somewhat higher hydrophobicity resulting from lengthening of the *N*-alkyl group.

In recent years, molecular recognition has been attracting wide attention. Most studies of molecular recognition have been based on complementarity between host and guest molecules in size, polarity, etc. [1–6]. On the other hand, it is well-known that many kinds of ionic dye interact with oppositely charged polyion to aggregate [7–9]. It is inferred that the guest dyes could be recognized by host polymer according to the difference in molecular structure of the dyes, if the host has an appropriate recognition site according to, for example, size, polarity, planarity or a combination of these. For example, Okhata *et al.* [10], reported that certain kinds of dye can intercalate into the double helix of DNA. In this case, molecular planarity of the dyes is one of the important factors, as well as the hydrophobicity and the positioning of two amino groups. Separation of triphenylene and *o*-terphenyl has also been investigated chromatographically in terms of steric selectivity using an alkylated stationary phase [11, 12].

In our previous paper [13], we reported that methylene blue (MB) and acridine orange (AO) could be incorporated into anionic bilayer aggregates of L-**1** in the crystalline state. However, since crystal violet and a bulky cyanine dye (NK-737) did not show such behaviour, it is suggested that the anionic bilayer membranes in their crystalline state could incorporate only a certain kind of cationic dye and that these bilayer membranes have selectivity. These results were an indication of molecular recognition and prompted us to investigate the structural features of these cationic dyes concerning hydrophobicity and molecular planarity. However, it is difficult to compare the structural features of many kinds of dyes, because these dyes have different hydrophobicity which plays a crucial role in hydrophobic interactions with aqueous molecular assemblies. The other reason is that it is difficult to assign the absorption bands of dye species because the aggregated dyes often give plural absorption bands according to the differences in aggregation number and stacking angle [14]. Thus, to

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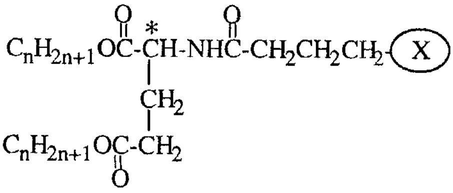
* Author for correspondence.

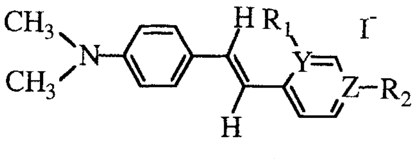
interpret the position systematically, dyes which ordinarily show no aggregation behaviour, but solvatochromism, have been chosen. In this communication, we report a recognition ability of the average molecular planarity of cationic dyes by anionic bilayer aggregates **1**–**3**.



1, $n = 18, X = -S-(CH_2-\underset{COO^-Na^+}{CH})_{7.2}-H$

2, $n = 18, X = COO^-Na^+$

3, $n = 16, X = COO^-Na^+$



4, $Y = C, R_1 = H, Z = N^+, R_2 = CH_3$

5; $Y = N^+, R_1 = CH_3, Z = C, R_2 = H$

6, $Y = N^+, R_1 = C_2H_5, Z = C, R_2 = H$

Amphiphile L-**1** was prepared as reported previously [13]. Amphiphiles L- and DL-**2**, and L- and DL-**3** were prepared in a similar way to that reported previously [13], using glutaric anhydride instead of succinic anhydride. The chemical structures were determined by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR), and confirmed by elemental analyses. Formation of bilayer aggregates of all amphiphiles in water was confirmed by transmission electron microscopy (TEM) and supported by differential scanning calorimetry (DCS) measurements. All cationic dyes were purchaesed from the Aldrich Chemical Co., Inc. and recrystallized from methanol. The purity of all dyes was confirmed by paper chromatography. All the solutions were prepared by adding 1 ml ($4{\cdot}65 \times 10^{-3}$ mol l^{-1}) of an aqueous stock solution of dye to independently prepared aqueous dispersions (30 ml) of the appropriate amphiphiles and sonicated with heating. After the solutions had been allowed to stand at 20°C, the pH was adjusted to 10 by adding aqueous sodium hydroxide. The solutions thus prepared were used for the measurements of the visible absorption spectra.

Figure 1 shows the typical absorption spectra of the cationic dye, 4-(4-N, N-dimethylaminostyryl-*N*-methylpyridinium iodide (**4**) in various media. The dye **4** showed absorption maxima (λ_{max}) at 448 nm in water and 476 nm in methanol, regardless of temperature and concentration. These phenomena are ascribable to solvatochromism. When anionic bilayer membranes of L-**1** were added to the aqueous solution, λ_{max} shifted from 448 nm to 473 nm at 20°C. This suggests that dye **4** was incorporated into the relatively apolar microenvironment, close to that of methanol, presumably the hydrophobic region of the bilayer aggregates at 20°C. The λ_{max} at 473 nm shifted drastically to 450 nm at the phase transition temperature (T_c; peak-top temperature in DSC for the gel to liquid crystal transition) of L-**1** aggregates on heating to the liquid crystalline state, suggesting that dye **4** transferred to the polar region to bind to carboxylate. These considerations could be supported by additional experimental results; when poly(sodium acrylate), which cannot produce hydrophobic sites to incorporate hydrophobic dye and generally induces aggregation of cationic dyes, is used instead of L-**1**, the λ_{max} of dye is **4** located at around 448 nm, close to that in pure water, regardless of both temperature and molar ratio of carboxylate to dye **4**. The fluorescence intensity of dye **4** in aggregates of L-**1** is about twice that in pure water and methanol at 20°C. These two additional results shows that dye **4** has no λ_{max} shift resulting from aggregation or thermochromism, suggesting that dye **4** is incorporated into the hydrophobic region of L-**1** aggregates in their crystalline state. The simplified compounds **2** and **3** showed similar behaviours to that of L-**1** aggregates. This indicates that this specific incorporation of the dye is not peculiar to the bilayer membranes formed from telomer amphiphile L-**1**.

To clarify the effect of average, molecular planarity of the dyes on incorporation into bilayer aggregates, due **5** which has a ring *N*-methyl group at the 2-position and has restricted free rotation of the pyridinium ring compared with dye **4** was investigated. As shown in figure 2, dye **4** had λ_{max} at 482 nm corresponding to that in organic solvents at 20°C and showed a hypsochromic shift to 438 nm upon heating up to the liquid crystalline state. The absorption band at 438 nm is slightly hypsochromic as compared with that at 448 nm for dye **4** alone in water, probably due to the absorption bands by aggregates with head to head stacking [14] induced by binding to highly ordered carboxylates. On the other hand, dye **5** showed a slight λ_{max} shift to 443 nm, close to that in pure water, in the presence of bilayer aggregates of **3** at 20°C. This indicates that dye **5** is harder to be incorporate than **4** into the hydrophobic region of the bilayer aggregates. Since the difference in chemical structure between **4** and **5** is only the position of the *N*-methyl group, the difference in hydrophobicity is considered to be practically negligible. Therefore, it is suggested that preferential incorporation of dye **4** is closely related to the average molecular planarity of the dye.

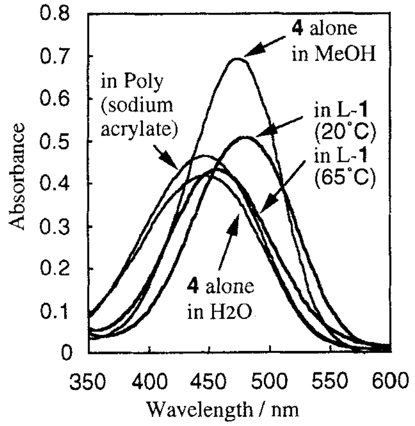


Figure 1. Typical absorption spectra of **4** in various media [concentration] [**4**] = 1·5 × 10^{-4} mol l^{-1} = constant, pH 10·0. [L−**1**] = 6·0 × 10^{-4} mol l^{-1}, [COO^-]/[**4**] = 29. Temperature; 20°C and 65°C.

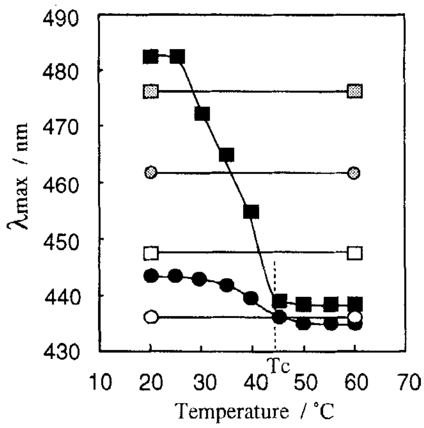


Figure 2. Temperature dependencies of λ_{max} of dye **4** in the presence of bilayer aggregates of L – **3**. [concentration] $[\mathrm{L-3}]=6{\cdot}0\times10^{-4}\,\mathrm{mol\,l^{-1}}$, $[4]=1{\cdot}5\times10^{-4}\,\mathrm{mol\,l^{-1}}$, pH 10·0. Dotted lines indicate the peak-top temperature (T_c) of L – **3** in DSC. (■), **4** in L – **3**; (▨), **4** in MeOH; (◉), **5** in MeOH; (□), **4** in H_2O; (●), **5** in L – **3**; (○), **5** in H_2O.

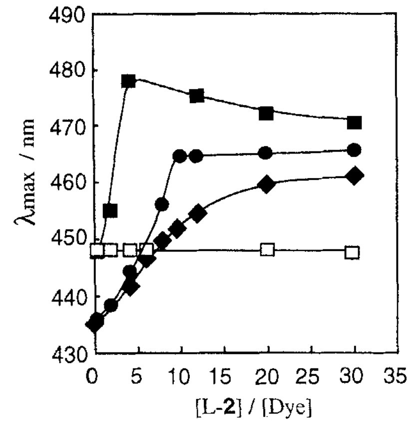


Figure 3. Variation of molar ratio of L – **2** to dye at fixed concentration of dye. [concentration] $[\mathrm{dye}]=1{\cdot}5\times10^{-4}\,\mathrm{mol\,l^{-1}}$, pH 10·0, 20°C. Molar ratios of poly(sodium acrylate) to dye indicate residue ratios $[\mathrm{COO^-}]/[\mathrm{dye}]$. (■), dye **4**; (●), dye **5**; (◆), dye **6**; (□), poly(sodium acrylate) and dye **4**.

Next, the contribution of hydrophobicity to incorporation was investigated using bilayer aggregates of L-**2**. In general, increasing the molar ratio of amphiphile to dye promotes the transition of dye species from aggregates to monomer by incorporating them into the hydrophobic region, and the λ_{max} value reaches a constant value close to those in organic solvents. As shown in figure 3, the λ_{max} of dye **5** reaches a constant value at a molar ratio of around 10, whereas dye **6** which has the *N*-ethyl group at the 2-position reaches a constant value at a molar ratio around 20, indicating that dye **6** is harder to incorporate than **5**, in spite of its somewhat higher hydrophobicity. In general, it is considered that the higher the hydrophobicity of a dye, the easier the dye is incorporated into the hydrophobic region of bilayer aggregates. Thus, these antithetical behaviours suggest that the average molecular planarity predominates over hydrophobicity in determining preferential incorporation of dye **4** over dye **5**.

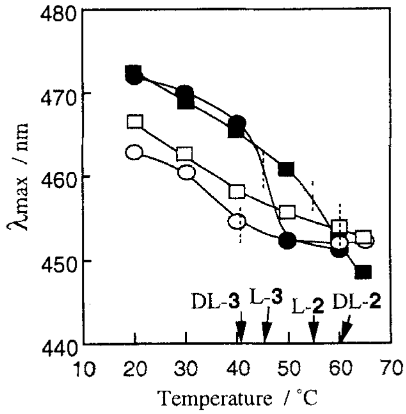


Figure 4. Temperature dependencies of λmax of dye **4** in the presence of L-isomer and DL-mixture. (■), L−**2**; (●), L−**3**; (□), DL−**2**; (○), DL−**3**. The dotted lines and the arrows on *x* axis indicate the peak-top temperature (T_c) in DSC. [concentration] [**4**] = 1·5 × 10^{-4} mol l^{-1}, [Amphiphile] = 6·0 × 10^{-4} mol l^{-1}, pH 10·0.

Furthermore, DL-**2** and DL-**3** were investigated to confirm that dye **4** exists near the glutamate residue in the crystalline state. As shown in figure 4, the λ_{max} of due **4** in DL-**2** and DL-**3** aggregates at temperatures below T_c were obviously different from those in L-**2** and L-**3** aggregates, respectively, indicating that the packing mode among neighbouring glutamate residues is different and influences the dye incorporation. No crucial difference of transition enthalpy (ΔH) values between aqueous dispersion of L-isomers and DL-mixtures was observed by DSC measurements: ΔH values were about 9 kcal mol^{-1} for **2** and about 8 kcal mol^{-1} for **3**. These results suggest that the dye exists near the glutamate residue of respective bilayer aggregates.

In conclusion, the mechanism of selective incorporation behaviours by anionic crystalline bilayer aggregates are ascribable to the average molecular planarity of the dyes. Such a specific behaviour seems to be based on the fitting of the planarity of the dyes to the hydrophobic site of crystalline molecular assemblies with appropriate molecular packings. This is the first evidence of planarity recognition of cationic dyes using anionic crystalline bilayer aggregates. Further investigations are in progress.

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