Supramolecular Thermochromism of a Dye-appended β-Cyclodextrin

Tetsuo Kuwabara,* Asao Nakamura, Akihiko Ueno* and Fujio Toda*

Department of Bioengineering, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

A β-cyclodextrin derivative **1** bearing a dye moiety reveals thermochromism; the mechanism is based on an equilibrium shift in its host–guest complexation, occurring in the range 25–65 °C in a 10% ethylene glycol aqueous solution.

Thermochromism, which is the reversible dependence of colour on temperature, has been studied with bianthorone,[1,2] spiropyran[3,4] and other organic compounds,[5–8] each existing in a thermal equilibrium between two distinct and interconvertible isomeric species. Previously, we have shown that methyl red-modified β-cyclodextrin **1** (Scheme 1) acts as a guest responsive colour change indicator for molecules.[9] In the course of our investigation, we found a novel thermochromic phenomenon, which occurs in solution on the basis of supramolecular complexation of **1**.

Figs. 1 and 2 show the absorption spectra of **1** in the presence of adamantan-1-ol (9.0×10^{-4} mol dm^{-3}) as a guest at various temperatures and the temperature-dependence curves of the absorbance at 540 nm of **1**, alone and in the presence of adamantan-1-ol (9.0×10^{-4} and 3.0×10^{-4} mol dm^{-3}), respectively. The absorption spectrum of **1** in the presence of adamantan-1-ol at pH 1.61 at 25 °C exhibits a band with a maximum at 503 nm, indicating that the methyl red moiety is excluded from the cavity by adamantan-1-ol and exists in the azonium form.[10] The absorbance around 500 nm was reduced and the absorption maximum of **1** was blue shifted with increasing temperature, suggesting that the azonium form of **1** is converted into the azo form. Only a slight hypochromic effect was observed when the solution of methyl red at pH 3.8 (*ca.* 93% of methyl red exists as the azonium form) was heated. So this conversion of **1** from the azonium into the azo form may be interpreted in terms of the inclusion of the methyl red moiety into the cyclodextrin (CD) cavity. Consequently, the guest accommodated inside the cavity of **1** is excluded to the outside of the cavity as shown in Scheme 1. As a result, we observed an orange colour at 65 °C but on cooling to 25 °C, the solution reverted to the original red colour. This cycle can be repeated more than several times without any indication of decomposition of the components. Furthermore the solution of **1** alone did not change its colour upon heating, although a slight hyperchromic effect was observed, demonstrating that the methyl red moiety, which is included in the CD cavity at 25 °C, remains as the azo form even at higher temperatures. From this finding it can be concluded that this thermochromism occurs based on host–guest complexation of **1** with the guest species. When the concentration of adamantan-1-ol added is less (3.0×10^{-4} mol dm^{-3}), the colour of the solution of **1** at 25 °C is orange and turned to yellow on heating to 65 °C. Similar results were obtained when other guests, such as cyclohexanol and (−)-borneol, were used in place of adamantan-1-ol.

To confirm the structural feature of **1**, we measured the induced circular dichroism spectra of **1** in the absence and presence of adamantan-1-ol at 25 and 55 °C. The solution of **1** exhibits a positive band around 420 nm at both 25 and 55 °C,

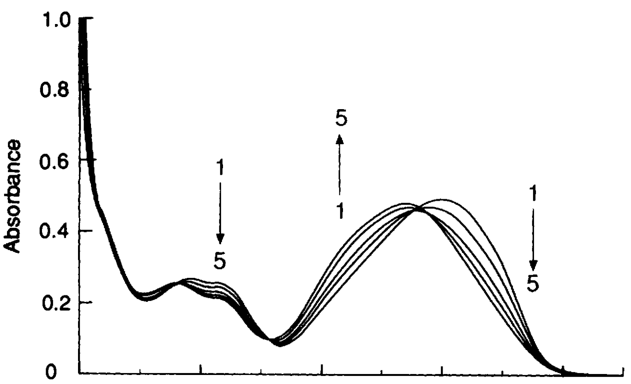


Fig. 1 Temperature-induced absorption variations of **1** (3.0×10^{-5} mol dm^{-3}) in the presence of adamantan-1-ol (9.0×10^{-4} mol dm^{-3}) at pH 1.61 at 25 °C in a 10% ethylene glycol aqueous solution: (1) 25, (2) 35, (3) 45, (4) 55 and (5) 65 °C

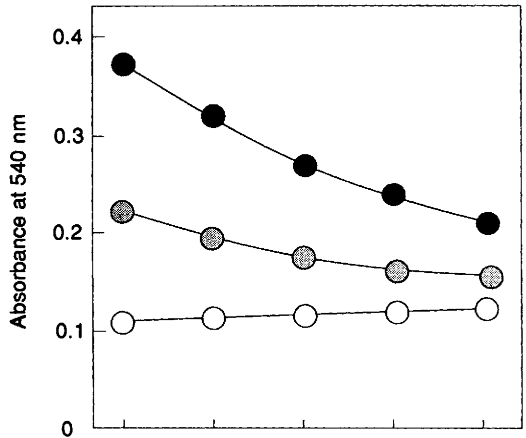
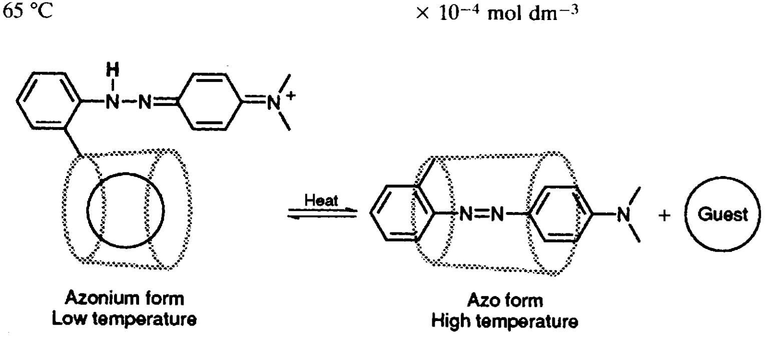


Fig. 2 Temperature-dependence curve of absorbance at 540 nm, at various concentrations of adamantan-1-ol: ○, 0; ◍, 3.0×10^{-4}; ●, 9.0×10^{-4} mol dm^{-3}



Scheme 1

associated with methyl red π–π^* transition,[11] with the value of $[\theta]$ of 2230 and 1970, respectively. This result suggests that the methyl red moiety is included in the CD cavity mainly orientated parallel to the CD axis at both temperatures.[12] On adding adamantan-1-ol at 25 °C, however, the intensity of the band decreased with a value of $[\theta]$ of 1370 and a new negative band appeared at *ca.* 500 nm, which is in the absorption region of the azonium form. This result suggests that the methyl red moiety included as the azo form in the CD cavity is excluded to the outside of the cavity by adamantan-1-ol so as to be oriented perpendicularly to the CD axis as the azonium form. A similar spectral change was observed on addition of adamantan-1-ol at 55 °C. The change in the spectra, however, was smaller than at 25 °C. The decrease of the dichroism intensity at 420 nm by the guest addition relative to its original value gives the ratio of **1** which is existing as the inclusion complex with adamantan-1-ol. On this basis, *ca.* 45% and *ca.* 30% of **1** were estimated to form the inclusion complex with adamantan-1-ol at 25 and 55 °C, respectively. This result suggests that it is difficult for **1** to form the inclusion complex at high temperature as compared with low temperature. In other words, the intermolecular complex of **1** with the guest is converted into the intramolecular complex by heating. This conformational change of **1** induces the conversion of the methyl red moiety from the azonium form into the azo one, resulting in the colour change.

In conclusion, the thermochromism occurs based on the equilibrium shift in the host–guest complexation of **1**. Many other thermochromic systems will be produced on this principle.

Received, 28th September 1993; Com. 3/05827A

References

1 Y. Tapushi, O. Kalisky and I. Agranat, *J. Org. Chem.*, 1979, **44**, 1949.

2 K. Maeda, T. Miyahara, T. Mishima, S. Yamada and Y. Sano, *J. Chem. Soc., Perkin Trans. 2*, 1984, 441.

3 B. Hellrung and H. Balli, *Helv. Chim. Acta*, 1989, **72**, 1583.

4 Y. Sueishi, M. Ohcho and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2608.

5 J.-H. Fuhrhop and D. Fritsch, *J. Am. Chem. Soc.*, 1984, **106**, 4287.

6 K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 429.

7 S. Nakada, T. Ito, M. Yamada and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2913.

8 Y. Sakaino, R. Fuji and T. Fujiwara, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2852.

9 A. Ueno, T. Kuwabara, A. Nakamura and F. Toda, *Nature*, 1992, **356**, 136.

10 S. Yamamoto, N. Nishimura and N. Hasegawa, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 194.

11 J. Kroner and H. Bock, *Chem. Ber.*, 1968, **101**, 1922.

12 K. Harata and H. Uedaira, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 375.