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Inclusion complexes of poly-β-cyclodextrin with 2-anilino-6-naphthalenesulfonic acid, 1-chloronaphthalene, and azulene in aqueous solutions

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Abstract

In aqueous solutions, 2-anilino-6-naphthalenesulfonic acid (2,6-ANS), 1-chloronaphthalene (1CN), and azulene (Az) form 1:1 inclusion complexes with a β-cyclodextrin (β-CD) moiety in poly-β-cyclodextrin (poly-β-CD). Equilibrium constants (*K*) for the formation of the inclusion complexes have been evaluated from the fluorescence intensity changes with concentration of poly-β-CD. The *K* values for poly-β-CD are similar to those for β-CD. In contrast to the behavior of β-CD whose 1:1 inclusion complexes with 1CN self-associate to form a 2:2 inclusion complex, the association does not occur between the β-CD moieties on the same poly-β-CD chain, indicating that poly-β-CD exhibits a rather simple inclusion mode. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Poly-β-cyclodextrin; Inclusion complexes; 2-Anilino-6-naphthalenesulfonic acid; 1-Chloronaphthalene; Azulene

1. Introduction

Cyclodextrins (CDs) are torus-shaped, cyclic oligosaccharides composed of six, seven, and eight D-glucopyranose residues, which are called α-, β-, and γ-CD, respectively. Because CDs have a relatively hydrophobic cavity in molecular center, a variety of organic compounds can be incorporated into their cavities to form inclusion complexes in aqueous solutions.

There are several studies on the complexation of β-CD polymers with guests. Using immobilized β-CDs which have been cross-linked with 1,2-ethanediol diglycidyl ether, etc., Sugiura et al. [1] have investigated the inclusion complexation of immobilized β-CDs with cresols, phenol, nitrophenols, and 2-naphthol. These guests form 1:1 inclusion complexes with a β-CD residue in immobilized β-CD. Harada et al. [2] have revealed that a 2:1 β-CD moiety–2-*p*-toluidinylnaphthalene-6-sulfonate (TNS) inclusion complex is exclusively formed for poly(acryloyl-β-CD). At a high concentration of β-CD, a 2:1 β-CD–TNS inclusion complex is formed, whereas a 1:1 β-CD–TNS inclusion complex is observed at a low concentration of β-CD. The interactions of polymeric CDs with pyrene have been studied by several researchers. For the systems of pyrene–polymers linked with epichlorohydrin, Xu et al. [3] have proposed a model involving sequential 1:1 and 2:1 clam shell binding with a second β-CD on the same polymer chain. Werner et al. [4] have indicated that the pyrene lifetimes show much greater dependence on iodide quencher concentration in the presence of CD polymers (CD units joined by repeating glyceryl linkers) than in the presence of β-CD and γ-CD. They have concluded that pyrene binding to the CD polymers may be largely noninclusional, involving considerable participation of the glyceryl linker units. They have also investigated the interactions of the CD polymers with three naphthalene-based fluorescence probes (2-acetylnaphthalene etc.) [5]. Hollas et al. [6] have suggested that poly(allylamine) with pendant β-CD groups exhibit a significant change in the complexation behavior depending on the degree of substitution. At high degree of substitution, a 2:1 β-CD moiety–pyrene inclusion complex was intramolecularly formed, while, at low degree of substitution, the 2:1 complex is intermolecularly formed.

In spite of these studies, complexation of CD polymers with guests has not been extensively examined compared to monomeric CDs. Poly-β-CD is a polymer of β-CD cross-linked with epichlorohydrin. Poly-β-CD is structurally different from polymers which have β-CD cavities as a pendant group. The presence of the linker (epichlorohydrin residue) may vary physicochemical properties of the inclusion complexes, because the linker likely restricts to some extent the movement of the β-CD moiety and because it likely affords a

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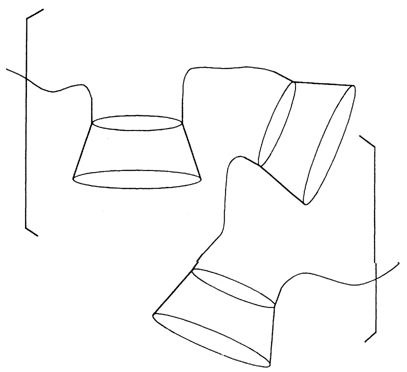
slightly different environment to a guest bound to the β-CD moiety. Consequently, the inclusion behavior of poly-β-CD is interesting from the viewpoints of not only the properties of the polymer but also the interactions of the β-CD moiety. Thus, we studied the inclusion complexation of poly-β-CD with 2-anilino-6-naphthalenesulfonic acid, 1-chloronaphthalene, and azulene, which were selected as guests forming a 1:1 β-CD–guest inclusion complex, a 2:2 β-CD–guest inclusion complex, and a ternary β-CD–alcohol–guest inclusion complex, respectively, and compared the results with those for monomeric β-CD.

2. Experimental details

2.1. Materials

β-CD obtained from Nakalai Tesque was twice recrystallized from water. Poly-β-CD purchased from Tokyo Kasei Kogyo, whose nominal degree of polymerization was 4–5, was dialyzed using UC24-32-100 dialysis tubing (Viskase Sales). The average molecular weight per one β-CD moiety in poly-β-CD was taken to be 1244 on the basis of an elemental analysis: calculated for $C_{45}H_{73}O_{36}\cdot 3H_2O$: C, 43.44; H, 6.40; found: C, 43.96, H, 6.97. A schematic representation of a part of poly-β-CD is shown.



Schematic representation of a part of poly-β-CD

2-Anilino-6-naphthalenesulfonic acid (2,6-ANS) was purchased from Molecular Probes, 1-Chloronaphthalene (1CN) obtained from Tokyo Kasei Kogyo was percolated through a silica gel column. Azulene (Az) from Tokyo Kasei Kogyo was chromatographed with a silica gel column.

2.2. Apparatus

Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence spectra were taken with a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. The fluorescence spectra were corrected for the spectral response of the fluorometer. Spectroscopic measurements were made at 25±0.1°C.

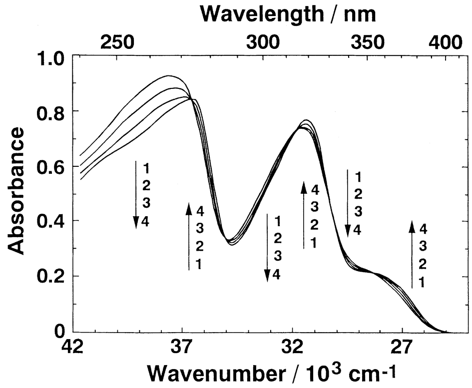


Fig. 1. Absorption spectra of 2,6-ANS (4.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. Concentration of poly-β-CD (β-CD moiety): (1) 0, (2) 1.0×10^{-4}, (3) 3.0×10^{-4}, and (4) 1.0×10^{-3} mol dm^{-3}.

3. Results and discussion

3.1. Inclusion complex between poly-β-CD and 2-anilino-6-naphthalenesulfonic acid (2,6-ANS)

Fig. 1 shows absorption spectra of 2,6-ANS (4.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. When poly-β-CD is added to 2,6-ANS solutions, the absorption maxima are shifted to longer wavelengths, accompanied by a slight increase in the peak absorbance of the 315 nm band and isosbestic points at 274, 285, 312, 332, and 352 nm. The absorption spectral changes indicate the formation of a 1:1 inclusion complex of 2,6-ANS with a β-CD moiety in poly-β-CD. Because there are several β-CD moieties in poly-β-CD, more than one 2,6-ANS molecule may be bound to multiple inclusion sites (β-CD moieties) in poly-β-CD, even when the 1:1 inclusion complex of 2,6-ANS with the β-CD moiety in poly-β-CD is formed.

$$(\beta\text{-CD})_p + 2,6\text{-ANS} \overset{K}{\rightleftharpoons} (\beta\text{-CD})_p \cdot 2,6\text{-ANS} \qquad (1)$$

where K is the equilibrium constant for the formation of the 1:1 inclusion complex, and $(\beta\text{-CD})_p$ and $(\beta\text{-CD})_p\cdot$2,6-ANS represent the single β-CD cavity on a poly-β-CD chain and the 1:1 inclusion complex of 2,6-ANS with the β-CD moiety in poly-β-CD, respectively.

Fig. 2 exhibits absorption spectra of 2,6-ANS (4.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Upon the addition of β-CD, the absorption maxima are shifted to longer wavelengths, accompanied by a decrease in the peak intensity of the 315 nm band and isosbestic points at 280 and 368 nm, indicating the formation of a 1:1 inclusion complex between β-CD and 2,6-ANS. The spectral changes caused by the addition of poly-β-CD and β-CD are different from each other, as revealed by the different wavelengths of the isosbestic points for poly-β-CD and β-CD. Because all parts of

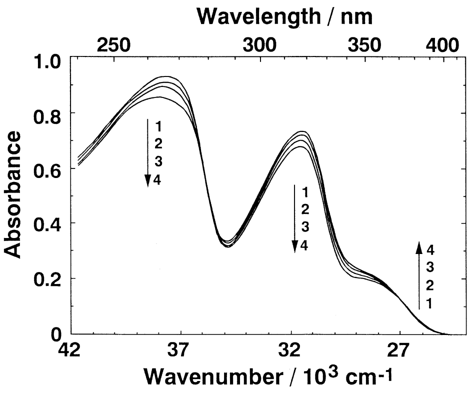


Fig. 2. Absorption spectra of 2,6-ANS (4.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-4}, (3) 3.0×10^{-4}, and (4) 1.0×10^{-3} mol dm^{-3}.

2,6-ANS do not enter the β-CD cavity, there is a polymer chain around a part of 2,6-ANS protruding from the β-CD cavity in poly-β-CD. Consequently, the absorption spectra of 2,6-ANS in the presence of poly-β-CD are most likely influenced by the environment around the β-CD cavity on a poly-β-CD chain. In the case of β-CD, on the other hand, a protruding part of 2,6-ANS is surrounded by the bulk water. Such a different environment around the protruding part of 2,6-ANS results in the different absorption spectral changes for the poly-β-CD and β-CD solutions.

Fig. 3 illustrates fluorescence spectra of 2,6-ANS in aqueous solutions containing various concentrations of poly-β-CD. When poly-β-CD is added, the fluorescence intensity of 2,6-ANS is considerably enhanced, accompanied by a blue shift of the peak. The enhancement in the integrated fluorescence intensity is 53-fold at a poly-β-CD (β-CD moiety) concentration of 1.0×10^{-3} mol dm^{-3}, whereas that is 16-fold at the same β-CD concentration. The K value for poly-β-CD was evaluated to be 2100 ± 600 mol^{-1} dm^3 from a double reciprocal plot for the fluorescence intensity change (not shown) [7,8]:

$$1/(I_f - I_f^0) = 1/a + 1/(aK[\text{poly-}\beta\text{-CD}]_0). \tag{2}$$

Here, I_f, I_f^0 , a, and $[\text{poly-}\beta\text{-CD}]_0$ are the fluorescence intensity in the presence of poly-β-CD, that in the absence of poly-β-CD, a constant, and the initial concentration of poly-β-CD, respectively.

The K value for β-CD was evaluated to be 1730 ± 20 mol^{-1} dm^3, which is slightly less than a literature value (2080 mol^{-1} dm^3) [9]. Although the K value for poly-β-CD is similar to that for β-CD, the enhancement of the fluorescence intensity for poly-β-CD is about three times greater than that for β-CD. In the case of 1,8-ANS, the formation of the 1:1 inclusion complexes with β-CD and its derivatives similarly leads to the enhancement of the 1,8-ANS fluorescence intensity [10]. This result has been explained in terms of the polarity of the CD cavity; the lower the cavity polarity is, the stronger the 1,8-ANS fluorescence intensity is. The same would be true for 2,6-ANS. The greater enhancement of the 2,6-ANS fluorescence for poly-β-CD solution suggests a less polar environment of 2,6-ANS bound to the β-CD moiety compared to monomeric β-CD. As previously stated, the absorption spectral changes (Fig. 1) for poly-β-CD solution are definitely different from those (Fig. 2) for monomeric β-CD solution. This suggests that terminal parts of an epichlorohydrin linker (residue) may extend the depth of the β-CD cavity to some extent and/or that there may be a linker chain near a protruding part of 2,6-ANS bound to the β-CD moiety in poly-β-CD. Even when poly-β-CD does not aggregate, therefore, the cross-linkage of epichlorohydrin between β-CD molecules likely provides a less polar environment for 2,6-ANS bound to the β-CD moiety.

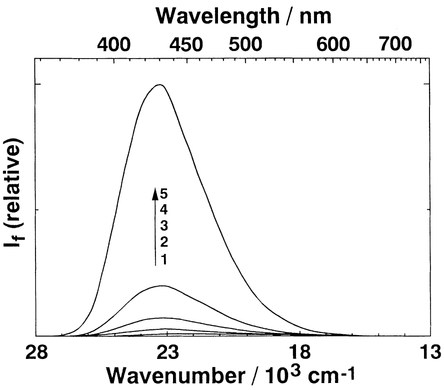


Fig. 3. Fluorescence spectra of 2,6-ANS (2.0×10^{-5} mol dm^{-3}) in aqueous solutions containing poly-β-CD. Concentration of poly-β-CD (β-CD moiety): (1) 0, (2) 1.0×10^{-5}, (3) 3.0×10^{-5}, (4) 1.0×10^{-4}, and (5) 1.0×10^{-3} mol dm^{-3}. λ_{ex}=314 nm.

3.2. *Inclusion complex between poly-β-CD and 1-chloronaphthalene (1CN)*

Fig. 4 exhibits absorption spectra of 1CN (5.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. As the concentration of poly-β-CD is increased, the absorption peaks are shifted to longer wavelengths, accompanied by a slight increase in the maximum absorbance and isosbestic points at 274, 278.5, and 284 nm. This finding indicates the formation of a 1:1 inclusion complex of 1CN with a β-CD moiety in poly-β-CD. On the other hand, upon the addition of β-CD to 1CN solutions, the absorption spectra of 1CN are shifted to longer wavelengths, with a drastic decrease in the absorption intensity and a significant blurring of the vibrational structures (Fig. 5) [11]. In addition, the absorption spectra of 1CN in aqueous β-CD solutions do not show isosbestic points at around 250 nm. In the presence of β-CD, a 2:2 β-CD–1CN inclusion complex has been found to be formed by the self-association of 1:1 β-CD–1CN inclusion complexes [11]. As in the case of the 2:2 β-CD–naphthalene inclusion

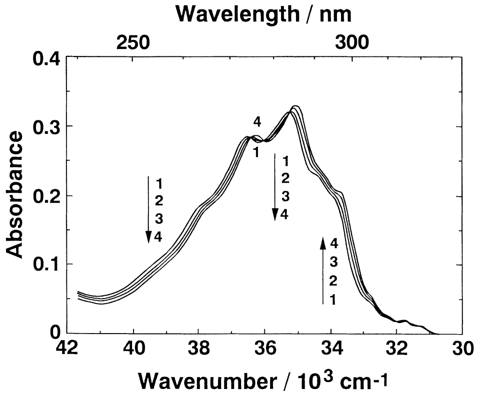


Fig. 4. Absorption spectra of 1CN (5.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. Concentration of poly-β-CD (β-CD moiety): (1) 0, (2) 3.0×10^{-4}, (3) 1.0×10^{-3}, and (4) 3.0×10^{-3} mol dm^{-3}.

complex [8], the 2:2 β-CD–1CN inclusion complex exhibits the 1CN excimer fluorescence.

In aqueous 1CN solutions with poly-β-CD, an interchain association between the 1:1 inclusion complexes would not occur because of the low concentrations of 1CN and poly-β-CD. Consequently, the result that only the 1:1 inclusion complex is formed between 1CN and the β-CD moiety in poly-β-CD suggests that the 1:1 inclusion complex cannot associate intramolecularly with another 1:1 inclusion complex on the same poly-β-CD chain, probably because a polymer chain cross-linked to β-CD sterically obstructs the association of the 1:1 inclusion complexes. Such a behavior of poly-β-CD may depend on the degree of polymerization of poly-β-CD. For pyrene, Xu et al. [3] have proposed that a 1:1 β-CD moiety–pyrene inclusion complex associates with a second β-CD moiety on the same polymer chain. In this respect, further study would be necessary.

The addition of β-CD to a 1CN solution leads to both the decrease in the 1CN monomer fluorescence and the appearance of the 1CN excimer fluorescence [11]. Fig. 6 depicts fluorescence spectra of 1CN in the absence and presence of poly-β-CD (3.0×10^{-3} mol dm^{-3}). In contrast to β-CD, the 1CN monomer fluorescence is enhanced by the addition of poly-β-CD. In addition, it does not induce the 1CN excimer fluorescence. As shown by the absorption spectral changes in Fig. 4, the fluorescence spectral changes in Fig. 6 also indicate that, in poly-β-CD solutions of 1CN, the 1:1 inclusion complex alone is present as an inclusion complex. From the intensity change in the 1CN monomer fluorescence, the *K* value for poly-β-CD is evaluated to be 670±50 mol^{-1} dm^{3} (Fig. 7). For β-CD, the *K* value has been estimated to be 868 mol^{-1} dm^{3} from a simulation method for the 1CN excimer fluorescence intensity [11]. The error of the *K* value for β-CD has been estimated to be less than 10%. Taking into account the errors, these *K* values are similar to one another.

It should be noted that poly-β-CD behaves a rather simple inclusion mode in contrast to β-CD whose inclusion complex with 1CN exhibits complicated inclusion modes, i.e., the self-association of the 1:1 inclusion complexes as well as the 1:1 inclusion complexation.

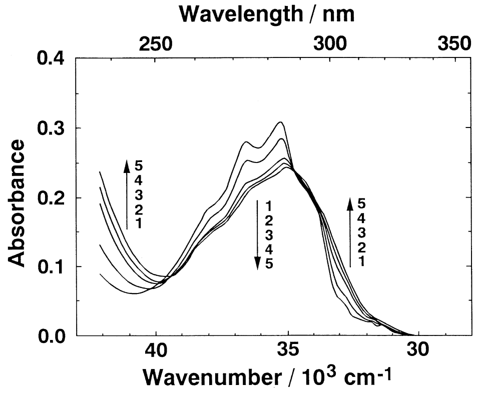


Fig. 5. Absorption spectra of 1CN (5.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-4}, (3) 1.0×10^{-3}, (4) 2.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

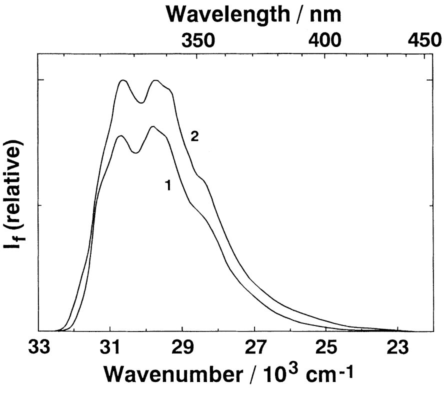


Fig. 6. Fluorescence spectra of 1CN (2.5×10^{-5} mol dm^{-3}) in aqueous solutions in the absence and presence of poly-β-CD (β-CD moiety) (3.0×10^{-3} mol dm^{-3}). λ_{ex}=295 nm.

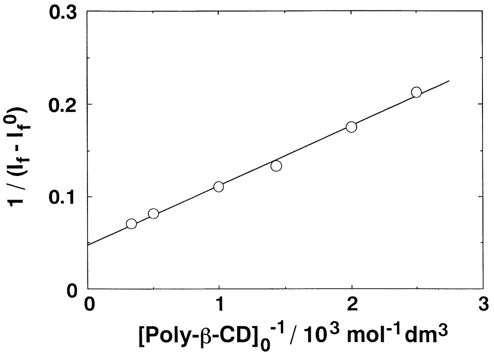


Fig. 7. Double reciprocal plot for the 1CN (2.5×10^{-5} mol dm^{-3}) monomer fluorescence in aqueous solutions containing poly-β-CD. λ_{ex}=295 nm. λ_{obs}=337 nm.

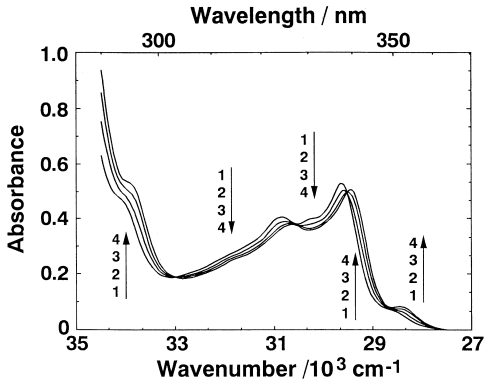


Fig. 8. Absorption spectra of Az (1.2×10^{-4} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. Concentration of poly-β-CD (β-CD moiety): (1) 0, (2) 5.0×10^{-4}, (3) 2.0×10^{-3}, and (4) 5.0×10^{-3} mol dm^{-3}.

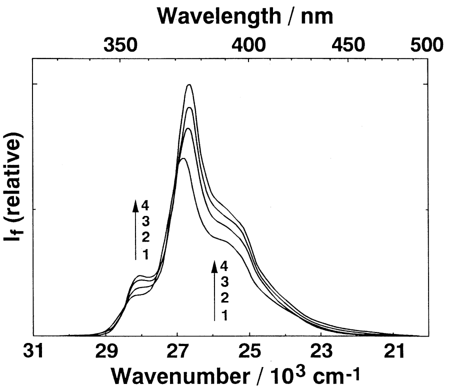


Fig. 10. Fluorescence spectra of Az (8.0×10^{-6} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. Concentration of poly-β-CD (β-CD moiety): (1) 0, (2) 5.0×10^{-4}, (3) 2.0×10^{-3}, and (4) 5.0×10^{-3} mol dm^{-3}. λ_{ex}=278 nm.

3.3. Inclusion complex between poly-β-CD and azulene (Az)

Figs. 8 and 9 respectively show absorption spectra of the $S_0\rightarrow S_2$ and $S_0\rightarrow S_3$ bands of Az (1.2×10^{-4} and 4.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. As the poly-β-CD concentration is increased, the absorption bands are shifted to longer wavelengths, accompanied by isosbestic points at 274.5, 278, 279.5, 302.5, and 309 nm. This finding indicates the formation of a 1:1 inclusion complex of Az with a β-CD moiety in poly-β-CD. When β-CD has been added to Az solutions, on the other hand, the isosbestic points have also been observed, but at different wavelengths of 245, 280.5, 306, and 339 nm [12]. These results suggest that, in spite of the deep penetration of Az into the β-CD cavity in poly-β-CD, Az experiences an environment different from that Az bound to the monomeric β-CD cavity does. Consequently, Az seems to interact slightly with a poly-β-CD chain through the open mouths of the β-CD moiety. Alternatively, there may be the possibility that the conformation of the β-CD moiety in poly-β-CD is varied by the substitution at the hydroxyl group (s).

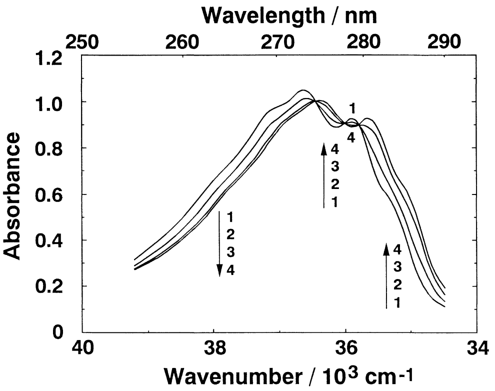


Fig. 9. Absorption spectra of Az (4.0×10^{-5} mol dm^{-3}) in aqueous solutions containing various concentrations of poly-β-CD. Concentration of poly-β-CD (β-CD moiety): (1) 0, (2) 5.0×10^{-4}, (3) 2.0×10^{-3}, and (4) 5.0×10^{-3} mol dm^{-3}.

Fig. 10 exhibits fluorescence spectra of Az in aqueous solutions containing various concentrations of poly-β-CD. With an increase in the poly-β-CD concentration, the fluorescence intensity is increased, and the fluorescence is slightly red shifted. From the double reciprocal plot for the fluorescence intensity changes (not shown), the K value for poly-β-CD has been evaluated to be 670±80 mol^{-1} dm^3, which is similar to the K value (520±100 mol^{-1} dm^3) for β-CD [12].

As previously reported, a ternary inclusion complex of β-CD–alcohol–Az, which includes two β-CD molecules, is formed [12]. The addition of 1-propanol to an Az solution containing β-CD results in a sharpened absorption spectrum of Az and a sharpened and enhanced fluorescence spectrum of Az [12]. Thus, we examined the effect of 1-propanol on the absorption and fluorescence spectra of Az in poly-β-CD solution. The shape of the Az fluorescence spectrum was not varied by the addition of 1-propanol (0.134 mol dm^{-3}). In addition, only about 2% enhancement of the fluorescence intensity was observed. Consequently, there is little or no formation of the ternary inclusion complex among a β-CD moiety, 1-propanol, and Az. This finding is consistent with the result that no self-association occurs between the 1:1 β-CD moiety–1CN ((β-CD)$_p$–1CN) inclusion complexes.

4. Concluding remarks

In aqueous solutions, 2,6-ANS, 1CN, and Az form 1:1 inclusion complexes with a β-CD moiety in poly-β-CD. The K values for poly-β-CD are respectively similar to those for β-CD. Consequently, the polymer chain in poly-β-CD does not affect the magnitudes of the K values. However, the absorption spectral changes of 2,6-ANS and Az upon the addition of poly-β-CD are definitely different from those upon the addition of β-CD, suggesting some interactions between the guests incorporated into the β-CD cavity and the polymer chain. Alternatively, the conformation of the β-CD moiety in poly-β-CD may be slightly varied by the substitution of the polymer chain.

The 1:1 β-CD–1CN inclusion complexes associate to form a 2:2 β-CD–1CN inclusion complex, which emits the 1CN excimer fluorescence [11]. The 1CN excimer fluorescence, however, is not observed for poly-β-CD solution of 1CN. Consequently, the association between the β-CD moieties on the same polymer chain does not occur for the inclusion complex of poly-β-CD with 1CN. Similar association between different kinds of inclusion complexes has been examined; for the poly-β-CD–1-propanol–Az system, there is no evidence for the formation of the ternary inclusion complex of $(\beta\text{-CD})_p$–1-propanol–Az, although the ternary inclusion complex of β-CD–1-propanol–Az, which includes two β-CD molecules, has been observed [12]. Therefore, the association between the 1:1 inclusion complexes of the same or different kinds does not occur on the same polymer chain of poly-β-CD, whose degree of polymerization is nominally 4–5.

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