Complexation and Photodimerization of Anthracene-2-sulfonate in the Presence of Per-6-aminocyclodextrins

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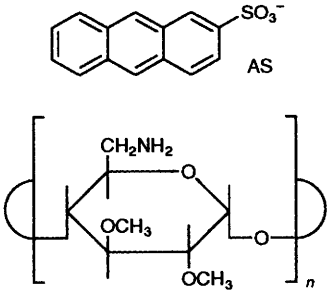
The stoichiometry of molecular complexation of anthracene-2-sulfonate (AS) with hexakis-, heptakis- and octakis-(6-amino-2,3-di-*O*-methyl-6-deoxy)cyclodextrins (α-, β- and γ-PACDs) has been investigated by UV, fluorescence, and circular dichroism spectrophotometry; in neutral and alkaline media only β-PACD gives the 2:2 inclusion complex, while in sufficiently acidic media all PACDs form the inclusion complexes by benefitting greatly from electrostatic interactions. The relative rates for the PACD-promoted photodimerization are closely related to the complexation modes.

Supramolecular assemblies have been the subject of intensive investigations in many aspects of chemical, biological and pharmaceutical sciences.[1] Particularly, the versatility of cyclodextrins interacting with substances has been widely recognized to afford possibilities of constructing artificial enzymes in biomimetic chemistry, since cyclodextrins † (CDs) have a cavity capable of accommodating a wide variety of organic and inorganic compounds in aqueous solution through hydrophobic and van der Waals interactions. In such complexes the hydrophobic portion of a guest molecule makes contact with the apolar wall of the CD. It has been demonstrated that host–guest complexation presents a selective feature in some reactions since the size of the cavity determines a complexation stoichiometry; recently anthracene-2-sulfonate (AS) has been



n = 6 α-PACD
7 β-PACD
8 γ-PACD

reported to undergo rapid photodimerizations in the presence of β- and γ-CDs to yield a mixture of four different stereoisomers with head/tail and *syn*/*anti* configurations, as a result of predominant formation of the 2:2 and 1:2 CD–AS complexes, respectively, while the presence of α-CD with a smaller cavity did not affect the rate of the photodimerization.[2] As compared with such parent CDs, however, the versatility of functionalized CDs has not been well recognized yet, although controlling the binding interactions through functionalization of natural CDs is very promising for designing complexes with appropriate stability and desired catalytic activity.

In this paper, we report our studies on the inclusion complexation and the photochemical behaviour of anthracene-2-sulfonate in the presence of a set of cyclodextrins carrying amino groups at the primary face (α-, β-, γ-PACDs); such peramino functionalization would be expected to enhance greatly the ability of CDs to bind acidic substrates by electrostatic interactions as an additional binding force and thereby might cause marked changes in both complexing and photochemical processes. Recently, we have demonstrated that such PACD derivatives exhibit a high binding affinity toward oxalacetate in the decarboxylation reaction.[3]

We have now found that the PACDs exhibit intriguing behaviour in photodimerization and complexation events, significantly different from those of the parent CDs.

Experimental

Materials.—α-, β- and γ-CDs purchased from Tokyo Kasei Co. were dried *in vacuo* (1 Torr‡/100 °C) for 24 h before use. Anthracene-2-sulfonic acid (AS) was prepared according to a literature procedure;[4] sodium anthraquinone-2-sulfonate was reduced with Zn powder in 30% aq. ammonia at 60 °C, followed by recrystallization from dimethylformamide (DMF)–CH_3CN, giving yellow leaflets; δ_H(400 MHz; H_2O–DMSO 1:1; Me_4Si) 7.60 (2 H, m, 6, 7-H), 7.72 (1 H, m, 3-H), 8.15 (3 H, m, 4-, 5-, 6-H), 8.43 (1 H, s, 1-H), 8.62 (1 H, s, 10-H) and 8.68 (1 H, s, 9-H). Hexakis-, heptakis- and octakis-(6-amino-2,3-di-*O*-methyl-6-deoxy)-cyclodextrins (α-, β- and γ-PACDs, respectively) were synthesized from the corresponding per-6-bromocyclodextrins according to a method described by Lehn *et al.*[5] The starting materials 6-bromo-6-deoxycyclodextrins were prepared by modifying the method of Takeo.[6]

CD:*AS Molar Ratio Determination.*—The molecular stoichiometries of complexation were determined by a combination of UV—or circular dichroism (CD)—photometric and fluorimetric titrations in unbuffered neutral water, 0.1 mol dm^{-3} HCl–KCl buffer of pH 1.0 or 2.2 and 0.1 mol dm^{-3} carbonate buffer of pH 10.0. With increasing concentrations of PACD, the UV-absorption intensity at the longest wavelength (378 nm) decreased depending upon the nature of the PACD used, since an AS molecule makes contact with the PACD cavity. In order to determine the equilibrium association constants (K_a), UV-titrations were performed by stepwise addition of aliquots from a 2.0×10^{-2} mol dm^{-3} stock solution of PACDs to 3 cm^3 of a 2.0×10^{-4} mol dm^{-3} AS solution. Ten to fifteen points were taken for each determination until at least a ten-fold excess of the host was achieved. Binding constants were obtained by using the convenient eqns. (1)–(4). These equations were derived according to the same numerical

† α-, β-, γ-Cyclodextrin = cyclomalto-hexaose, -heptaose, -octaose.

‡ 1 Torr ≈ 133 Pa.

$$[AS]_0[CD]_0/(A - A_0) = 1/K_a\Delta\varepsilon + ([AS]_0 + [CD]_0)/\Delta\varepsilon \quad \text{for a 1:1 CD–AS complex} \quad (1)$$

$$[AS]_0^2[CD]_0^2/(A - A_0) = 1/K_a\Delta\varepsilon + 4[AS]_0[CD]_0([AS]_0 + [CD]_0)/\Delta\varepsilon \quad \text{for a 2:2 complex} \quad (2)$$

$$[AS]_0[CD]_0^2/(A - A_0) = 1/K_a\Delta\varepsilon + [CD]_0(4[AS]_0 + [CD]_0)/\Delta\varepsilon \quad \text{for a 2:1 complex} \quad (3)$$

$$[CD]_0[AS]_0^2/(A - A_0) = 1/K_a\Delta\varepsilon + [AS]_0(4[CD]_0 + [AS]_0)/\Delta\varepsilon \quad \text{for a 1:2 complex} \quad (4)$$

treatment as described in the literature.[2a] $[AS]_0$ and $[CD]_0$ are the initial concentrations of AS and CD, respectively. CD denotes any of the CD derivatives. K_a is the equilibrium constant for the formation of the complex. A and A_0 are the absorbance measured in the presence and absence of the host, respectively.

Fluorescence spectra were taken using the excitation wavelength of 250 nm and the monitoring wavelength of 415 nm corresponding to the maximum of the AS emission band. In all cases examined, there was no change in the shape of the bands but there was a decreasing change in the intensity of the fluorescence spectrum on increasing addition of PACD. The spectra were analysed by the same numerical treatment as in the case for the UV spectra, where an assumption was made that any complex species are non-fluorescent. In order to make a correction for deviation from the Lambert–Beer linearity law, the observed relative emission intensity ($F/F_0 = I$) was transformed into the apparent, relative concentration ($I = [AS]/[AS]_0$) by using a calibration curve obtained by plotting the emission intensities *vs.* the known concentrations of AS. The processed data are shown in Table 2. UV and fluorescence spectra were recorded on a Hitachi 220A spectrophotometer and a Shimadzu RF-5000 spectrofluorophotometer, respectively.

Kinetics of AS Photodimerization.—Photodimerization was carried out as follows: a 2.0×10^{-4} mol dm^{-3} solution of AS was placed in a UV cell and was flushed with nitrogen for 10 min. The solution was continuously photoirradiated at 0 °C in the presence or absence of PACDs with a 150 W Xe-lamp by using a filter which cuts out light below 300 nm. The absorption band due to AS disappeared completely and that of the photodimer appeared at a wavelength shorter than that of AS. Rates were measured on a Hitachi 200A spectrophotometer and rate constants were calculated from the decrease of the absorbance (λ_{max}) of AS after irradiation. The results thus obtained are summarized in Table 1 and Fig. 4. For HPLC determination of product distributions, the reaction solutions were pretreated as follows; the reaction solution was neutralized with NaOH and then the PACD was extracted out with $CHCl_3$ and the aqueous layer was freeze-dried and subsequently analysed by HPLC on an octadecylated silica gel reverse column using 80% MeCN–H_2O as an eluent.

Induced Circular Dichroism (ICD).—Spectra were recorded on a JASCO J-720 spectropolarimeter under the same conditions as in the case of the photodimerization study. Some typical spectra are displayed in Fig. 2 and their characteristic aspects are summarized in Table 3. The molar ratio for the inclusion complexes was determined by means of Job's method of continuous variations. In this procedure the first component, PACD, was varied from 0% to 100%, while the second component, AS, was varied from 100% to 0%, the total molar concentrations remaining constant (1.0×10^{-3} mol dm^{-3}).

Table 1 Effect of addition of PACDs on the rate of AS photodimerization in H_2O at 0 °C[a]

Additive	$k_{obs}/10^{-2}$ min	λ_{max}/nm	A (±0.01)
None	3.4	378	0.65
α-CD	2.2	378	0.64
β-CD	15.1	379	0.72
γ-CD	90.4	380	0.424
α-PACD	1.5	378	0.65
β-PACD	36.6	382	0.37
γ-PACD	3.6	378	0.65

[a] Conditions: $[AS] = 2.0 \times 10^{-4}$ mol dm^{-3}; $[CD] = 2.0 \times 10^{-3}$ mol dm^{-3}; under N_2 150 W Xe-lamp; 0 °C.

Results and Discussion

Complexing Modes in Neutral and Alkaline Media.—We have investigated, first, the photodimerization of AS in the presence of CDs and PACDs. The reaction takes place *via* an interaction of the $\pi \rightarrow \pi^*$ excited singlet state AS molecule with the ground state AS molecule.[7] In the cases of unmodified β- and γ-CDs the products' identities and composition have been established by Tamaki *et al.* to be a mixture composed of four possible stereoisomers with head/tail and *anti*/*syn* configurations.[2] Since the product distribution is critical for elucidating the mode of complexation, we also have attempted to determine the product distributions and the results will be discussed briefly in the last section.

When the efficiency of a photoreaction is examined in order to understand the dynamic features of the reaction, we use the initial rate instead of the quantum yield, since they are parallel to each other. In this work, however, the rate was calculated by postulating the first-order kinetics for convenience, because the concentration of AS decreased in a first-order manner for a substantial part of the reaction. The obtained first-order rate constants for the photodimerization in neutral water (pH 6.8) containing a ten-fold excess of parent CDs are summarized in Table 1; the rates were found to be in the decreasing order: γ-CD > β-CD ≫ α-CD ≈ none. This sequence was in good agreement with the previously reported quantum yields.[2] In particular, γ-CD accelerated the rate 27-times as compared with a reaction in its absence. Consistent with this result, addition of γ-CD caused a red-shift to 380 nm of the longest wavelength band centred at 378 nm with a considerable hypochromism as large as 35%.[8] This is an indication of an obvious intermolecular transannular π-electronic interaction between two aromatic ring faces in the ground state where the long axes of the ring faces experience a substantial degree of parallelism, since the magnitude of the spectral changes is related to the extent of overlap of the two fused rings.[9] On the other hand, an 11% hyperchromism with a weak bathochromism to 379 nm was found with β-CD, suggesting that the aromatic portion is positioned in hydrophobic surroundings (Table 1). Evidently, the kinetic and spectroscopic observations suggest a marked difference in the complexation mode between β- and γ-CDs; with the latter having a bigger cavity, a highly photoreactive 1:2 CD–AS complex is produced exclusively, in which the two AS molecules are stacked fully or appreciably, while the former gives rise to a 1:1 CD–AS complex. However, the relatively fast photodimerization (refer to Table 1) and the appearance of non-related isosbestic points imply that β-CD and AS form complexes with higher stoichiometric ratios besides a 1:1 complex even at such low CD and AS concentrations.[2] Tamaki

Table 2 Molecular stoichiometries and equilibrium constants (K_a) for CD–AS inclusion complexes at different pH values[a] (by UV or fluorometric titrations) (M = mol dm^{-3})

	α-PACD				β-PACD				γ-PACD			
pH	CD–AS[b]	λ/nm	A	K_a	CD–AS[b]	λ/nm	A	K_a	CD–AS[b]	λ/nm	A	K_a
1.0	1:1	386	0.62	4.1×10^2 M^{-1}	2:2	385	0.39	2.4×10^{10} M^{-3}	2:2	379	0.62	1.9×10^9 M^{-3}
	1:2[c]			7.7×10^5 M^{-2}[c]								
6.8	1:1[c]	378	0.65	2.1×10^3 M^{-1}[c]	2:2	382	0.37	4.4×10^9 M^{-3}	1:1[c]	378	0.65	2.8×10^3 M^{-1}[c]
10	1:1[c]	378	0.65	1.7×10^3 M^{-1}[c]	2:2	381	0.51	9.5×10^8 M^{-3}	1:1[c]	378	0.65	2.7×10^3 M^{-1}[c]

[a] [PACD]:[AS] = 10:1. [b] Molar ratio determined by taking into account both the kinetic and spectroscopic data. [c] Value determined fluorometrically.

et al. reached the same conclusion. Incidentally, neither rate enhancement nor spectroscopic change was detected with α-CD.

On the other hand, PACDs have different complexation and photodimerization properties from their corresponding parent CDs. The photodimerization rates with PACDs in neutral water are also listed in Table 1; the reaction sequence was β-PACD ≫ γ-PACD ≈ none ≥ α-PACD. Only β-PACD was effective. As expected, α-PACD slightly retarded the rate. Nevertheless, the lack of catalytic activity of γ-PACD was entirely unexpected.

In order to understand the photochemical behaviour of PACD molecular complexes, the ground-state complexing ability of these complexes was examined in detail by UV, CD and fluorescence spectroscopy, since the orientation and disposition of the complexed anthracene moiety with respect to the CD cavity is of particular importance in understanding the photochemical mechanism.

In all UV-spectrometric titrations, the concentration of AS was fixed at 2.0×10^{-4} mol dm^{-3} and that of PACDs was varied from 2.0×10^{-4} mol dm^{-3} to at least 2.0×10^{-3} mol dm^{-3} until the saturation of the peak height was attained. The absorbances decreased upon increasing concentrations of PACDs. Thus, the stoichiometric ratios could be determined from a data point set that affords a linear plot by applying any one of eqns. (1), (2), (3) and (4). Relevant data are summarized in Table 2.

In aqueous neutral solution containing varying amounts of β-PACD, as the β-PACD concentration increased, the absorption peak was red-shifted considerably, with an isosbestic point at 384 nm and a decreasing absorbance. The data points fitted eqn. (2) best; correlation factors of regression lines for 1:1, 2:2, 2:1 and 1:2 complexes were 0.854, 0.994, 0.993 and 0.854, respectively. Taken in combination, the calculated stoichiometry and the enhanced photodimerization rate suggest, therefore, that β-PACD forms a well-defined 2:2 molecular complex with AS. The evaluated aqueous binding constant (K_a = 4.4×10^9 mol^3 dm^{-9}) was 2.5 times greater than that reported for β-CD (K_a = 1.7×10^9 mol^3 dm^{-9}).[2] Such a slight but obvious increase in binding strength can be rationalized if an extra stabilizing force is combined with hydrophobic interactions; that is, the major component of the increased stability might dwell in electrostatic acid–base interactions rather than hydrophobic inclusion. However, no further valuable information about the detailed structure could be obtained from the UV spectra.

Unambiguous determination of the orientation and depth of the anthracene moiety in the cavity could be made with the help of CD spectroscopy.[10,11] Induced circular dichroic (ICD) spectra due to the longest wavelength π→π* transition of AS at pH 2.2, 6.8 and 10.0 are shown in Figs. 1(*a*)–(*c*) and their ICD signs are summarized in Table 3. As inspection of Fig. 1(*b*) reveals, only β-PACD among the PACDs exhibits an intense ICD curve with a positive first (375 nm) and a negative second (325 nm) Cotton effect due to an exciton coupling of the ^1L_a electronic transition and a negative (280 nm) and positive (240 nm) Cotton effect due to the ^1B_b transition (the ICD bands due to the ^1B_b transition are not shown in Fig. 1). There is a relationship between the Cotton effect sign and the molecular geometry. The positive to negative sign change for the β-PACD–AS complex is opposite to the negative to positive change for the γ-CD–AS complex, strongly indicating that the AS hydrocarbon portion protrudes from the β-PACD cavity to induce a Cotton effect opposite to that of the γ-CD complex, where the ^1L_a transition moment is polarized perpendicular to the CD-rotation axis and the ^1B_b transition moment is polarized parallel.[10] That is to say, the AS molecule sits only slightly in the CD cavity in the longitudinal direction probably because replacement of OH groups by NH_2 groups, with some of them existing in the hydrophilic ammonium form even under neutral conditions, reduces the hydrophobicity around the primary face of the cavity and its poorer inclusion ability toward the AS molecule results accordingly.

Table 3 ICD of PACD–AS complexes at different pH values at 385 nm[a]

	Intensity and polarity			
pH	α-PACD	β-PACD	γ-PACD	β-CD
2.2	− −	+ + +	+	0
6.8	0	+ +	0	−
10.0	0	+	0	−

[a] The number of + and − signs denotes the relative magnitude of a positive and a negative Cotton effect, respectively. [AS] = 2.0×10^{-4} mol dm^{-3}, [PACD] = 2.0×10^{-3} mol dm^{-3}.

Obviously, the occurrence of the exciton coupling is interpreted in terms of a pairing of AS molecules to give the 2:2 dimer associated by the primary faces. This implies that the formation of the 2:2 complex *vs.* 1:1 complex is favourable for β-PACD. The changes in the sign of the Davydov splitting from positive to negative for the ^1L_a band and negative to positive for the ^1B_b band may demonstrate that the paired AS molecules take an S-helix configuration. The two 1:1 monomeric units are held together by electro-attractive interactions between the sulfonate and ammonium groups as well as by a tighter stacking interaction between the aromatic rings, these forces giving the 2:2 complex greater stability than the 1:1 complex. Actually, unlike unmodified β-CD which forms the more deeply included AS complex [Fig. 2(*a*)], there is no spectroscopic evidence for the existence of the 1:1 β-PACD complex. Fig. 2(*b*) illustrates the most reasonable structure for the β-PACD–AS complex.

On the other hand, results obtained from fluorimetric titrations, which are also included in Table 2, seem to show that α- and γ-PACDs form a 1:1 contact ion-pair with AS, where the whole AS molecule is fixed at the outside of the CD cavity, as illustrated in Fig. 2(*c*). In accordance with this inference, no ICD was detected, demonstrating that the anthracene part lies in the region giving no ICD. Clearly, the inclusion of AS by α-PACD is impossible for steric reasons. More interesting is the unexpected photo-catalytic inefficiency of γ-PACD unlike γ-CD itself. The reason for its inefficiency remains unclear. No perceptible change in the UV absorption spectrum and no ICD was dis-

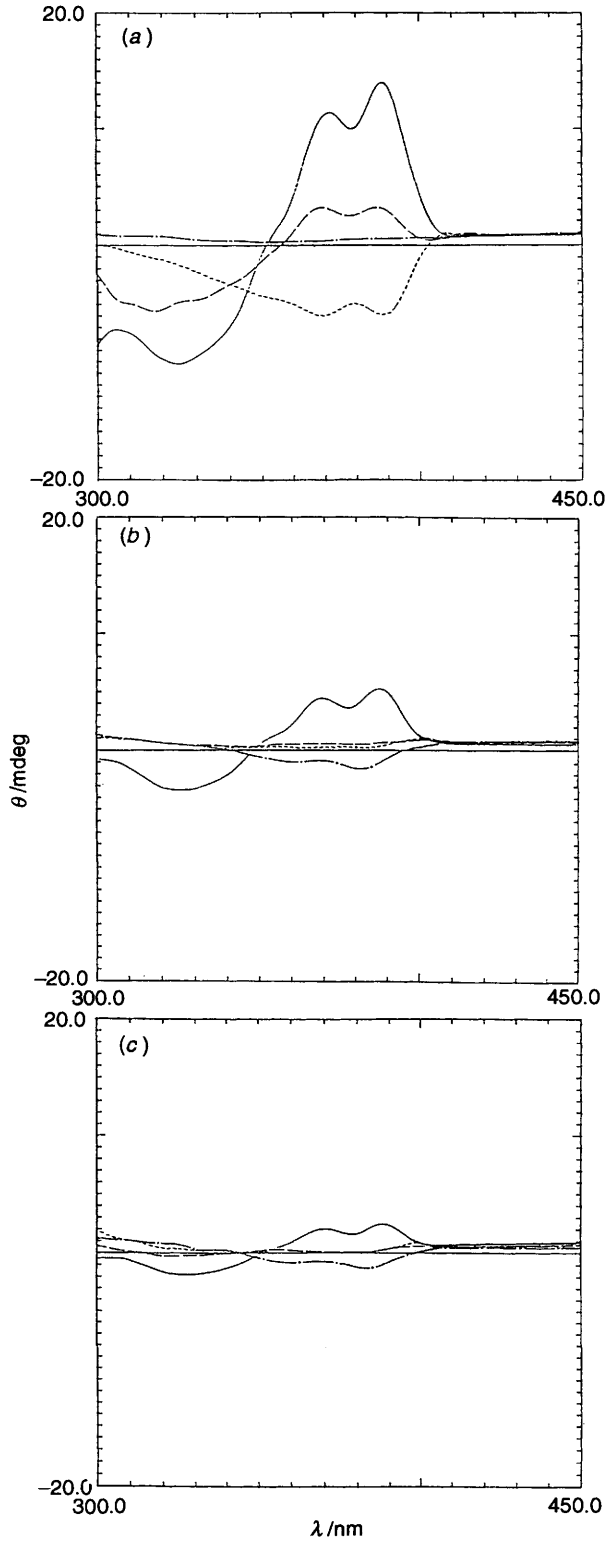


Fig. 1 CD spectra of PACD–AS and CD–AS complexes at (*a*) pH 2.2, (*b*) 6.8 and (*c*) 10.0; [AS] = 2.0×10^{-4} mol dm^{-3}, [α-, β-, γ-PACD] = 2.0×10^{-3} mol dm^{-3}: α-(– – –), β-(——), γ-PACD (— — —), β-CD (— · — · —)

cernible even at sufficiently high PACD concentrations, providing no physical evidence of inclusion, *i.e.* γ-PACD must bind an AS molecule only *via* an acid–base ion-pairing. Such a spectral observation of γ-PACD led us to the conclusion that an AS molecule is too small to fit the cavity size of γ-PACD and, furthermore, the PACD cavities become generally less hydrophobic than those of natural CDs.

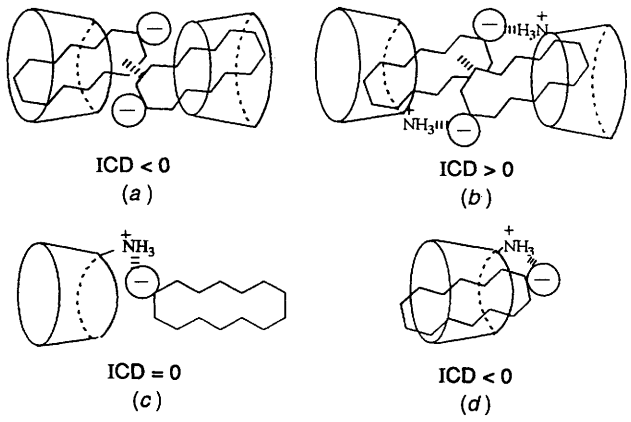


Fig. 2 Plausible structures of (*a*) β-CD–AS, (*b*) β-PACD–AS complexes and (*c*) ion-pairs of α- or γ-PACD with AS in neutral water. (*d*) Proposed structure of α-PACD–AS complex formed under sufficiently acidic conditions. An open circle (○) denotes an SO_3^- group.

Generally, PACD complexes do not emit fluorescence. This is attributable to a fast non-radiative process taking place in the complexes.[12] It may be inferred, therefore, that single electron transfer from the amino nitrogen to the photoexcited AS molecule in the contact ion-pair is responsible for fast fluorescence quenching, as was reported for quenching by amines of 9-cyanoanthracene fluorescence.[13] Of course, the same explanation would be generally adoptable to fluorescence quenching processes for other PACD–AS complexes. However, the binding constants (K_a) obtained, *i.e.* greater than 10^3 dm^3 mol^{-1} for α- and γ-PACD (Table 2), are too large for merely electrostatic stabilization in water.[14] Thus, we suppose that such apparently large K_a values cannot be attributable to the formation of a real contact ion-pair complex which predominates in non-aqueous media,[15] but to a dynamic radiationless process in a short-lived, encounter complex.

Complexing Modes in an Acidic Medium.—When the solution's pH was decreased to a sufficiently acidic region, pronounced changes in UV and ICD spectra were observed with all PACDs with an increase in their concentrations: the longest wavelength band (λ = 378 nm) was red-shifted in the decreasing order: α-PACD > β-PACD > γ-PACD > none. It is evident, therefore, that acidic conditions greatly enhanced the binding ability of PACD for AS as a result of the formation of salt bridges between the sulfonate anion and the rimmed ammonium cations.

As the PACD concentrations were raised, UV spectra for β- and γ-PACDs decreased progressively in intensity and reached saturation, while that for α-PACD decreased initially and then increased to a saturation level, giving a well-separated new band peaked at 386 nm with a clear isosbestic point at 382 nm.

From the UV titrations, the possible PACD–AS ratios were indicated to be 2:1 or 2:2 for β- and γ-PACD and 1:1 or 2:1 or 2:2 for α-PACD (these plots not shown here). Within experimental error, we could not determine which is the more preferred stoichiometry for each complex.

Meanwhile, examination of the ICD spectra enabled us to provide substantial information on these structures. The stoichiometries could be determined by Job's method based on the absorbance change at 380 nm, ([PACD] + [AS]) being kept constant (1.0×10^{-3} mol dm^{-3}); representative plots are given in Fig. 3. Any ICD intensities had their most significant extent at a 1:1 molar ratio.

By taking the photodimerization-rate order into consideration, *i.e.* β-PACD ≫ γ-PACD > none ≫ α-PACD (Fig. 4), the lack of photo-activity of the α-PACD complex can be verified by a 1:1 structure, since such a complexation would perfectly

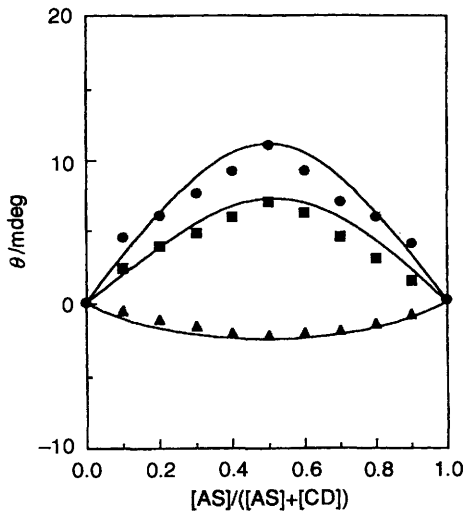


Fig. 3 Job's plots for (▲) α- and (●) β-PACD–AS complexes at pH 1.0 and (■) β-PACD–AS complex at pH 6.8; [AS] + [PACD] = 1.0 × 10^{-3} mol dm^{-1}

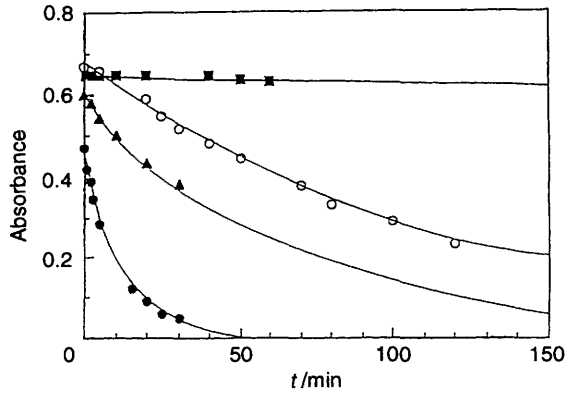


Fig. 4 Time-dependence of absorbance at λ_{max} for the AS photodimerization in the presence of PACDs at pH 2.2; [AS] = 2.0 × 10^{-4} mol dm^{-3}, [PACD] = 2.0 × 10^{-3} mol dm^{-3}, under nitrogen at 0 °C, 150 W Xe-lamp: α-(■), β-(●), γ-PACD (▲), absence of PACD (○)

prevent access of a second AS to the included AS molecule. Moreover, α-PACD exhibits a monosignate ICD curve with the same sign as that of the β-CD complex suggesting that the AS molecule is bound well into the inside of the α-PACD cavity, to the same extent as or to a greater extent than in the case of the β-CD complex. Thus, we can show pictorially the most plausible structure in Fig. 2(*d*). This may allow us to conclude further that the sulfonate anion on the AS molecule orients the rimmed ammonium groups in such a way as to maximize the stabilization of the anion–cation complexation by electrostatic attractions and thereby charge repulsion between the ammonium cations would be reduced. It has been well documented from NMR studies and inspection of CPK models that the aromatic hydrocarbon part in, *e.g.* naphthalene-2-sulfonate has great difficulty in getting into or protruding from the narrower end of the α-CD ring, forming, therefore, an only poorly embedded 1 : 1 complex on the wider end; thus, the α-CD complex is more than one order of magnitude less stable than the corresponding β-CD complex, but still more stable than the γ-CD complex.[16] Meanwhile, the remarkable red-shift with the α-PACD complex provides confirmation for the strong, penetrative 1 : 1 inclusion by a combined effect of hydrophobic and electrostatic bindings. Incidentally, the α-PACD–AS molar ratio determined by a fluorimetric method was 1 : 2, suggesting that most of the quenching takes place *via* an encounter complex formed between the 1 : 1 inclusion complex and a foreign AS molecule.

Meanwhile, the emergence of an exciton coupling for β-PACD shows that a 2 : 2 dimeric complex is formed with two AS molecules oriented anti-parallel to each other. Thus, the structural feature in acidic water is quite similar to that found in neutral water, as illustrated in Fig. 2(*b*). As predicted, the dimeric complex underwent a rapid stereospecific photodimerization (93%), giving rise to a head-to-tail photodimer with the sulfonate groups in the *anti*-position, while production of head-to-head dimers was not detected.

γ-PACD, at acidic pH, enhanced slightly the rate (1.7 times) (relative to its absence) and its AS complex exhibits a very weak positive, bisignate Cotton curve. The formation of a weaker 2 : 2 complex may be responsible for this result; namely, the complex is essentially close in structure to the corresponding β-PACD complex, but is less stable than it. In accordance with the above conclusions, the extent of the bathochromic shift is also fairly small probably owing to an inappropriate size fit between AS and the γ-PACD cavity.

In conclusion, spectroscopic and kinetic studies disclosed that the inclusion complexation of AS was observed only with β-PACD in neutral or alkaline medium, while in a fully acidic medium stronger inclusion occurs with the help of acid–base ion-pairing in all PACD molecules, even α-PACD molecule with the smallest cavity.

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