Inclusion Complexes of Pyrenylbutyrate with γ-Cyclodextrin

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Mixing 4-pyren-1-ylbutyrate ion with γ-cyclodextrin in aqueous solution leads to inclusion complexes that become evident from changed absorption spectra as well as protection of the included pyrene moieties from fluorescence quenchers. The inclusion proceeds in stages, yielding first a 1:1 complex, which then dimerizes to form a 2:2 complex. At 25 °C the respective equilibrium constants of complex formation are 1.3×10^3 and 5.2×10^4 l mol^{-1}. The dimerization equilibrium has an unusual temperature dependence, with $\Delta H^{\neq}$ −16.7 kcal mol^{-1} and $\Delta S^{\neq}$ −35 cal K^{-1} mol^{-1}.

Cyclodextrins are cyclic oligosaccharides, the most common of which (designated α, β, and γ) consist of six, seven, and eight glucose units, respectively. The internal cavities of these near-cyclindrical compounds range in diameter from 4.5 to 8.5 Å and can serve as hosts for guest molecules of appropriate size.[1] What makes cyclodextrins interesting is their ability, because their cavities are less polar than water, to extract, hold, and protect hydrophobic molecules from aqueous solution. Learning how to take advantage of these unique molecules is the object of much current chemical research.[1–7]

In continuation of our studies of medium-induced hydrophobic interactions,[8–10] we became interested in exploring the manner by which large aromatic molecules pack in a cyclodextrin cavity, the influence that such packing has on the photophysical properties of such molecules, and the protection that a cyclodextrin cavity provides to stabilize excited electronic states of the included molecules. As our large molecule we selected sodium 4-pyren-1-ylbutyrate (PB), a well established fluorescent probe we had used earlier. The fluorescence characteristics of PB are basically those of the pyrene moiety and include a long fluorescence lifetime and a distinct long-wavelength excimer fluorescence. The combination of a relatively large hydrophobic molecule with a water-soluble functional group seemed ideal for cyclodextrin work. The butyrate substituent permits reasonable concentrations of PB to dissolve in water, whereas the pyrene moiety prefers a hydrophobic host medium.

Utilization of the full range of the pyrene moiety's fluorescence capability required having cyclodextrin molecules with cavities large enough for two PB molecules. Inspection of CPK molecular models revealed that α- and β-cyclodextrin are too small, but that the next higher homologue in the cyclodextrin series will accommodate two pyrene molecules. For this reason we selected γ-cyclodextrin (γ-CD) in combination with PB for our investigations.

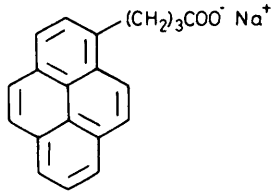
Results

Although the vibrational structure was retained, the absorption spectrum of a 5×10^{-7}M aqueous solution of PB shifted by 180 cm^{-1} to lower energy upon addition of γ-CD. Similar shifts could be effected for PB either by dissolving it in dioxane or by incorporating it into micelles. Furthermore, because substitution of glucose for γ-CD had no effect on the PB absorption spectrum, we conclude that the observed shift must be due to inclusion of PB by γ-CD.

The simplest possible complex between PB and γ-CD would have a 1:1 stoicheiometry and would be consistent with the absence of excimer fluorescence. Equations (1) and (2) specify

$$\text{PB} + \gamma\text{-CD} \overset{K_1}{\rightleftharpoons} \text{I} \qquad (1)$$

$$[\text{PB}]/[\text{I}] = 1/K_1[\gamma\text{-CD}] \qquad (2)$$



PB

the equilibrium and equilibrium constant involved with such a 1:1 complex.

Another change effected by γ-CD is the lengthening of the fluorescence lifetime of PB in deaerated solution from 120 to 145 ± 7 ns. However, both this increase in the fluorescence lifetime and the absorption shift are too small to allow accurate measurement of the I:PB ratios that are required for determination of the equilibrium constant K_1.

If we are dealing with included PB, then access to this species by an appropriate quencher (Q) should be hindered. The use of triethanolamine (TEA) in this context was revealing. This hydrophilic electron-transfer quencher† met the experimental requirement of not being included together with PB in γ-CD. To verify this point, we showed that the ratios φ_o/φ of PB fluorescence quantum yields and τ_o/τ of PB fluorescence lifetimes were equal. For both ratios the numerators were measured in the absence of and the denominators in the presence of TEA. It would have been ideal if the quencher were not included by itself in the cyclodextrin. However, K_1 still can be obtained if the equilibrium constant for the complex formation between Q and γ-CD is not large. At 25 °C with TEA at 3.6×10^{-2}M, the decay curve of a solution of 1.15×10^{-6}M-PB and 1.24×10^{-3}M-γ-CD showed two components with distinct lifetimes of 18 and 60 ns. Either the shorter lived or the longer lived species could be favoured by the respective lowering or raising of the γ-CD concentration. We conclude that the former is PB and the latter I. That the same concentration of TEA effects a larger decrease in the fluorescence lifetime of free PB than of PB in I reflects a lower rate of quenching of the latter, expected when PB is inside the cyclodextrin cavity and less accessible to TEA.

Figure 1 shows selected examples of these fluorescence decay data in the form of first-order plots of the logarithm of fluorescence intensity *versus* time. The four plots demonstrate a progressive shift from the 18 to the 60 ns species as γ-CD is added. When measurable quantities of both PB and I are present simultaneously as in the middle two decay curves of Figure 1, these curves can be used to measure the equilibrium

† TEA is assumed to behave like triethylamine as an electron donor.

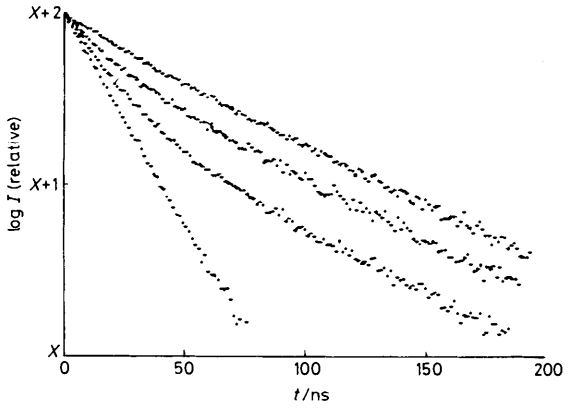


Figure 1. First-order plots of fluorescence decay of 1.15×10^{-6}M-PB with 3.6×10^{-2}M-TEA at 25 °C and monitored at 377 nm. In progressing from the fastest decay curve to the slowest, the γ-CD concentration increases from zero to 3.72×10^{-4}, 1.24×10^{-3}, and 1.00×10^{-2}M, respectively

concentrations of PB and I. This measurement involves analysing each decay curve into two components of the form $A_{PB}e^{-t/\tau_{PB}}$ and A_Ie^{-t/τ_I}, where the ratio of coefficients A_{PB}/A_I equals the ratio of the initial fluorescence intensities of each component. As given by equation (3), this ratio must be corrected for the different extinction coefficients of the two species as well as their different quantum yields of fluorescence in order to get the equilibrium ration [PB]/[I]. In equation (3)

$$\frac{[PB]}{[I]} = \left(\frac{A_{PB}}{A_I}\right)\left(\frac{\varepsilon_I}{\varepsilon_{PB}}\right)_{\lambda_{ex}}\left(\frac{Q_I}{Q_{PB}}\right)_{fl} \quad (3)$$

the ratio of extinction coefficients at the excitation wavelength of 337 nm is 0.78, and the ratio of fluorescence quantum yields is 1.05. This latter ratio was determined from solutions containing PB alone and with a high concentration of γ-CD to get mostly I and by exciting at 300 nm, a wavelength in a flat region of the absorption spectrum of pyrene where both PB and I have virtually identical extinction coefficients. The constancy of the ratio $[\gamma\text{-CD}]_o[PB]/[I]$ at various initial concentrations of γ-CD and at fixed quencher concentrations (*cf.* footnote *e*, Table) confirms formation of the 1:1 complex.

That rising TEA concentrations, despite a γ-CD concentration constant at 1×10^{-3}M, increase the ratio [PB]/[I] indicates that this quencher forms a complex with γ-CD as depicted by equation (4). At this low starting concentration of

$$Q + \gamma\text{-CD} \underset{}{\overset{K_Q}{\rightleftharpoons}} Q\cdot\gamma\text{-CD} \quad (4)$$

γ-CD, it can be shown that the concentration of uncomplexed γ-CD is given approximately by the expression (5). A linear

$$[\gamma\text{-CD}] \approx \frac{[\gamma\text{-CD}]_o}{1 + K_Q[Q]} \quad (5)$$

relationship between [PB]/[I] and [Q] is predicted by expression (6) and, with a plot of appropriate data from the

$$\frac{[PB]}{[I]} \approx \frac{1}{K_I[\gamma\text{-CD}]_o}(1 + K_Q[Q]) \quad (6)$$

Table, is realized in practice. From the intercept and the slope:intercept ratio of such a plot one can determine values for K_I and K_Q, respectively. To get the temperature dependence of these equilibrium constants, we carried out experiments at 45, 25, and 7 °C; K_Q had values of *ca.* 15, 12, and 8 l mol^{-1}, respectively, whereas the corresponding K_I values were 2 100, 1 280, and 820 l mol^{-1}. For the equilibrium of equation (1) we estimate $\Delta H^{\neq}$ −4.4 kcal mol^{-1} and $\Delta S^{\neq}$ −0.4 cal K^{-1} mol^{-1}.

Another component makes a small contribution to the total of monomer fluorescence from included PB. This component is less susceptible to quenching by TEA than is the fluorescence from I and is unlikely to be from impurities, because extensive additional purification of PB had no effect on this quantity or behaviour. The species responsible for this fluorescence could be another 1:1 complex in a different configuration and present at *ca.* 2% of the level of I. Traces of a 1:2 complex of PB and γ-CD also may be present. The value of the equilibrium constant for formation of the latter would have to be less than 1 l mol^{-1}.

In the absence of γ-CD, the absorption spectrum of PB between 5×10^{-7} and 2×10^{-4}M obeys Beer's law reasonably well. However, in the presence of γ-CD, higher PB concentrations effect profound changes from a well resolved to a poorly resolved spectrum. Much vibrational structure disappears, concomitant with a 500 cm^{-1} shift to lower energy and a loss in oscillator strength of *ca.* 25%.

At the same time that the absorption spectrum changes, the fluorescence spectrum shows a gradual replacement of the well structured pyrene monomer band by the structureless excimer band at longer wavelength. The influence of γ-CD is evident, because in its absence much higher concentrations of PB would

Lifetimes and ratios of I and PB in the deaerated solutions containing 1.08×10^{-5}M-PB, 1.01×10^{-3}M-γ-CD, and various concentrations of TEA

T/°C	[TEA]/M	τ_I/ns[a]	τ_{PB}/ns[b]	[PB]/[I][c]	K_Q/ l mol^{-1}[d]	K_I/ l mol^{-1}[d]
	0.0126	119	52	0.56		
7	0.0253	101	32	0.67	15	2 100
	0.0506	77	19	0.85		
	0.1012	51	11	1.21		
	0.0126	95	37	0.88		
25	0.0253	73	25	1.03	12	1 280
	0.0354[e]	60	18	1.14		
	0.0506	50	14	1.29		
	0.0126	71	27	1.36		
45	0.0253	48	15	1.44	8	820
	0.0354	36	11	1.58		
	0.0506	31	8.2	1.73		

[a] In the absence of TEA, the lifetime $(\tau_o)_I$ of I in deaerated solutions at 7, 25, and 45 °C are 155, 147, and 138 ns, respectively. These lead to quenching rate constants (k_q) of 1.3, 2.6, and 5.1×10^8 l mol^{-1} s^{-1}, respectively. These changes in k_q are due in part to changes in solvent viscosity and in part to the activation energy for penetration of the quencher to the interior of I. [b] In the absence of TEA, the lifetimes $(\tau_o)_{PB}$ of PB in deaerated solutions at 7, 25, and 45 °C are 133, 124, and 116 ns. These lead to quenching rate constants (k_q) of 9.0, 13.2, and 23×10^8 l mol^{-1} s^{-1}, respectively. These changes in k_q are due to different solvent viscosities at the three temperatures. [c] These ratios were determined from the corresponding relative intensities A_{PB}/A_I obtained from the fluorescence decay curves and multiplied by the correction factor 0.82 (0.78 × 1.05) from equation (3). [d] The equilibrium constants were determined from the linear plots of [PB]/[I] *versus* [TEA] according to equation (6). [e] For this quencher concentration at 25 °C and with several different γ-CD concentrations of 0.31, 0.61, and 1.00mM, τ_I and τ_{PB} remained constant at 61 ± 1 and 18.3 ± 0.4 ns, respectively, while the ratio [PB]/[I] gave values of 3.63, 1.84, and 1.14, respectively. However, because the product of $[\gamma\text{-CD}]_o$ and [PB]/[I] remained constant with respective values of 1.12, 1.12, and 1.14, the 1:1 stoicheiometry of complex I is confirmed.

be required to observe excimer fluorescence, and the excimer maximum in pure water is at slightly higher energy than when γ-CD is present. The addition of methanol to a concentrated aqueous solution of PB shifts the excimer band slightly to match that for PB in aqueous solution with γ-CD.

The combination of loss of absorption resolution and gain in excimer fluorescence is characteristic of ground-state interactions between pyrene moieties.[8-14] Association of two pyrene moieties with γ-CD would be required to explain these results. The simplest possible complex of this nature would have two PB molecules within one γ-CD cavity. For such a 2:1 complex, the ratio of fluorescence intensities at the excimer and monomer (PB plus I) maxima of 480 and 377 nm, respectively, would be expected to increase initially, reach a maximum, and then decrease with increasing γ-CD. What we observed instead was an initial sharp increase in this ratio followed by a slight increase above a γ-CD concentration of 1×10^{-2}M.

All experimental data point to the new species being a 2:2 complex formed through dimerization of the 1:1 complex according to equation (7). The equilibrium constant K_2 can be

$$2\,\mathrm{I} \overset{K_2}{\rightleftharpoons} \mathrm{II} \qquad (7)$$

$$K_2 = [\mathrm{II}]/[\mathrm{I}]^2 \qquad (8)$$

determined by applying equation (9) to absorption data.

$$K_2 = \frac{(\alpha - R)(\alpha - \beta)\left(1 + \dfrac{1}{[\gamma\text{-CD}]K_1}\right)^2}{2(R - \beta)^2[\mathrm{PB_o}]} \qquad (9)$$

Here R is the ratio of absorption intensities of any experimental solution at two different wavelengths, the second of which is an isosbestic point in the conversion of I into II. The terms α and β are the ratios at the same wavelengths in the spectra of I and II, respectively.* The actual wavelengths selected were 344 and 337.5 nm, respectively; the former is simultaneously a maximum in the spectrum of I and a shallow minimum in the spectrum of II, whereas the latter is an isosbestic point. For these wavelengths α is 2.30 and β is 0.67. The remaining term $[\mathrm{PB_o}]$ is the total concentration of free and complexed PB according to equation (10). K_2 values at 25 °C

$$[\mathrm{PB_o}] = [\mathrm{PB}] + [\mathrm{I}] + 2[\mathrm{II}] \qquad (10)$$

were measured for $[\mathrm{PB_o}]$ ranging from 5×10^{-6} to 2×10^{-4}M and are constant at 5.2×10^4 l mol^{-1} within 10% error.

Similar values for K_2 also were determined based on changes in fluorescence spectra brought about by adding γ-CD to various initial concentrations of PB.† The agreement in K_2 values determined for different $[\mathrm{PB_o}]$ and from both absorption and fluorescence data provides unambiguous proof of the validity of the equilibrium scheme of equations (1) and (7).

The absorption spectrum of 2.0×10^{-5}M-PB with 2.9×10^{-2}M-γ-CD changes dramatically with temperature. Figure 2 shows absorption spectra of this solution measured at four temperatures between 7 and 45 °C. These variations in spectra are due to an unusual temperature dependence of K_2, which drops from 3.5×10^5 at 7 to 5.3×10^3 l mol^{-1} at 45 °C. A plot of log K_2 *versus* $10^3\,T^{-1}$ in Figure 3 yields a straight line with a slope of 3.66, which translates to $\Delta H^{\ddagger}$ −16.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ −35 cal K^{-1} mol^{-1}.

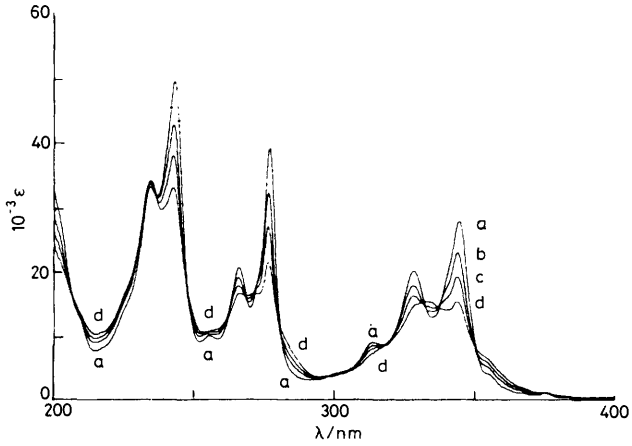


Figure 2. Absorption spectra of an aqueous solution containing 2.0×10^{-5}M-PB and 2.9×10^{-2}M-γ-CD at (a) 45, (b) 30, (c) 20, and (d) 7 °C

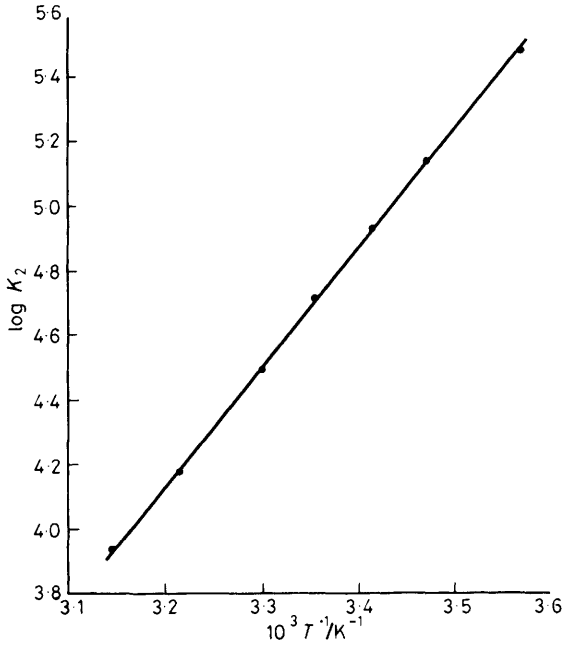


Figure 3. log K_2 *versus* $10^3\,T^{-1}$ for an aqueous solution containing 2.0×10^{-5}M-PB and 2.9×10^{-2}M-γ-CD

The actual absorption spectra of I and II are illustrated in Figure 4. In practice, mixtures of PB and γ-CD never yield pure I or pure II, but there is always some contamination from each other or from PB. The spectra in Figure 4 were derived from spectra measured for solutions containing mostly I and II, respectively, and corrections based on the individual equilibrium constants were applied to eliminate the minor components in the absorption. The derived absorption spectrum of II is very similar to the absorption spectrum of a solution containing >97% II (2.3×10^{-3}M-PB and 3.1×10^{-2}M-γ-CD, at 7 °C) and nicely matches the excitation spectrum (2.3×10^{-5}M-PB and 3.1×10^{-2}M-γ-CD at 25 °C) monitored at the excimer band maximum.

* At room temperature and with a γ-CD concentration of 3.0×10^{-2}M, a small quantity of uncomplexed PB remains in solution with I (in a ratio of 1:27). The term α was measured for this mixture.

† This method is more complex and will be reported in detail in a subsequent paper.

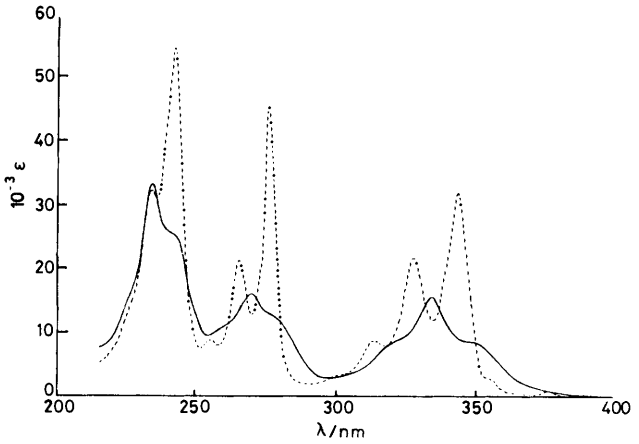


Figure 4. Absorption spectra of I (– – – –) and II (——) based on solutions containing PB and γ-CD at different concentrations and temperatures. Both spectra were corrected for competing absorption by small quantities of each other or PB present in the equilibrium mixtures

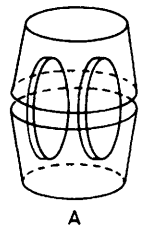
We have shown (Table) that at 25 °C singlet excited PB and I are quenched by TEA with rate constants of 1.3×10^9 and 2.6×10^8 l mol^{-1} s^{-1}, respectively. However, TEA, even at concentrations as high as 0.1M, does not measurably quench singlet excited dimeric complex II. Our quenching studies also extended to using molecular oxygen, for which, as with TEA, we demonstrated the absence of static quenching by measuring similar φ_o/φ and τ_o/τ values. Fluorescence lifetimes in argon- and oxygen-purged solutions at 30 °C show that the reaction constants for the oxygen quenching of PB, I, and II are 9.9×10^9, 4.5×10^9, and 1.4×10^9 l mol^{-1}, respectively.

The question arises whether excited-state equilibria could have affected the analysis given above. If the rate of formation and dissociation of the 1:1 complex involving excited PB were substantially higher than the excited-state decay rate (unimolecular decay and bimolecular quenching), only one component would have been detected in the monomeric fluorescence decay. If the inclusion of excited PB were slower, but still fast enough to compete with the quenching, there should be an apparent increase in the measured value for K_1 with increasing concentrations of γ-CD. The relevant data of Table, however, indicate no such trend. This behaviour is consistent with inclusion rate constants, mostly in the range 10^7—10^8 l mol^{-1} s^{-1} which are reported[15] for some large organic molecules in aqueous cyclodextrin solutions. Even if the reaction constant for inclusion of PB* in γ-CD were 10^8 l mol^{-1} s^{-1}, then at 0.01M-γ-CD this process will be less than 2% of the decay rate of PB* at the given quencher concentration (Table). The values of K_2 are derived from absorption spectra where these considerations do not apply.

Discussion

Two recent reports described fluorescence-based investigations of the inclusion complexes of molecular pyrene with γ-CD, but there was less than complete agreement between the two sets of results.[13,16] One group found that molecular pyrene and γ-CD join in 1:1, 1:2, and 2:1 complexes and estimated equilibrium constants for the formation of each,[13] whereas the other group claimed 1:1 and 2:1 complexes.[16]

Otagiri and his co-workers were the first to propose the 2:2 stoicheiometry for cyclodextrin inclusion complexes.[17] Edwards and Thomas looked at complex formation between molecular pyrene and β-cyclodextrin and also proposed 2:2 complex formation, but suggested that higher degrees of aggregation were possible.[18] Hamai, working with naphthalene and β-cyclodextrin, was the first to put a 2:2 complex on a firm basis, but he was unable to measure the thermodynamic state functions for the equilibrium leading to this complex.[14] Hamai noted that solubility restrictions prevented him from extending his investigation to complexes between molecular pyrene and γ-CD.



We circumvented the solubility problem of molecular pyrene by using PB; the pyrene moiety of this molecule retains most of the spectroscopic behaviour of molecular pyrene. We recognize that molecular pyrene and PB are distinct molecules and may not behave in precisely the same way upon inclusion by γ-CD. Our results show conclusively the formation as in equations (1) and (7) of the 1:1 complex followed by association to the 2:2 complex with no evidence for a 2:1 complex. We also observed no aging effects of the type reported by Edwards and Thomas[18] for complexation between molecular pyrene and β-cyclodextrin. An important discovery was the unusual thermodynamic behaviour of the equilibrium of equation (7).

A recent publication by Harada and Nozakura reports on the inclusion of sodium pyren-1-ylsulphonate (PS) by γ-CD.[19] The authors claim initial formation of a 1:1 complex followed by stepwise conversion first into a 2:1 complex and then into a 2:2 complex. This reaction scheme and the corresponding equilibrium constants of 1, 1×10^6, and 2×10^4 l mol^{-1}, respectively, were based on the results of computer simulation. We have investigated this system using our same experimental procedures described above and find that PS and γ-CD form 1:1 and 2:2 complexes by the same mechanism as PB and γ-CD and the two systems differ only in the sizes of the equilibrium constants. For PS and γ-CD we find K_1 and K_2 to be *ca.* 1.3×10^2 and *ca.* 1×10^6 l mol^{-1}, respectively, at 25 °C.

The computer simulation method[16,19] for determining equilibrium constants is risky and can lead to erroneous results even if the curve fitting appears to be good. By contrast, the measurement of fluorescence decay curves, particularly in the presence of quenchers, is a reliable method, because the individual components can be detected and their ratios accurately determined. A clear example of the pitfall of computer simulation is in the foregoing paragraph where, in the absence of other experimental support, the computer simulation value for K_1 is 1, whereas with direct detection of the individual species we find K_1 to be two orders of magnitude higher.

It is tempting to speculate about the structure of the 2:2 complex. γ-CD does not have a true cylindrical configuration[1] but is better depicted as being narrower at one end in the form of a truncated cone. Inspection of molecular models suggests that a 'barrel' configuration A is likely to be the most stable one to accommodate two pyrene moieties.

There may still be partial exposure of the included pyrene moiety in I to the surrounding aqueous medium, whereas such exposure inside the larger cavity of the 'barrel' should be minimal. The pyrene moieties achieving a more hydrophobic environment inside the 'barrel' may explain the large negative enthalpy change upon mating two I complexes. The associated large negative entropy change would be due to extensive

reordering of the individual PB molecules to get the pyrene moieties properly aligned.

The concept of protection by inclusion in cyclodextrin molecules goes back to Cramer in 1951, who found retarded autoxidation of benzaldehyde included by β-cyclodextrin.[20] Recent measurements of rate constants for luminescence quenching show substantial reductions after inclusion.[14,21] What we find in our quenching measurements is that the degree of protection increases from I to II and that the smaller quencher, molecular oxygen, can better penetrate to the included fluorescent species. The energetics of our fluorescence quenching are such that TEA should quench free PB reasonably efficiently,* whereas molecular oxygen should quench at the maximum possible rate. Because of the smaller size and the faster diffusion of oxygen, its maximum possible rate is greater than that for TEA.[25] The energy of fluorescent PB inside I should be almost the same as for free PB, and we find that the reduction in quenching efficiency is more than twice as large for TEA than for molecular oxygen. TEA at 0.1M does not measurably quench fluorescence from II, whereas oxygen still quenches this fluorescence at one-eighth its maximum rate. Questions now arise whether electron transfer from TEA to excited, aggregated pyrene moieties inside II is an endothermic process, or whether the inability of TEA to quench fluorescence from II is due largely to shielding effects of γ-CD. Although a positive answer to the latter question looks attractive at this point, we are seeking firm answers to both questions.

Experimental

We prepared PB by dissolving 4-pyren-1-ylbutyric acid (Kodak reagent grade) in 0.5M-sodium hydroxide solution, adding saturated sodium chloride solution to effect precipitation, filtering, and recrystallizing the PB from ethanol. PS (Molecular probes), γ-CD (Sigma Chemical Company), and TEA (Kodak reagent grade) were used as received.

All absorption spectra were measured on a Hitachi Perkin-Elmer model 320 spectrophotometer equipped with temperature-controlled cell holders. Fluorescence spectra and fluorescence lifetimes were measured with a Spex Fluorolog II spectrofluorimeter and a PRA fluorescence-lifetime apparatus, respectively. Fluorescence-liftime analysis of two-component systems was by the method of least-squares iterative reconvolution using the Marquardt algorithm;[26] the computer program was purchased from PRA.

* The oxidation potential of TEA and the reduction potential of PB are assumed to be matched by the corresponding potentials of triethylamine and molecular pyrene, respectively. The reversible oxidation potential of triethylamine is +1.19 eV *versus* n.h.e.[22] (corrected to +0.95 eV *versus* s.c.e.), the reduction potential of pyrene is 2.10 eV *versus* s.c.e.,[23] and the energy of the lowest excited singlet state of pyrene is 3.28 eV. From the Weller equation,[24] the $\Delta G^{\neq}$ value for electron transfer from TEA to PB is predicted to be −0.23 eV.

Acknowledgements

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References

1 M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,' Springer-Verlag, New York, 1978.
2 R. J. Bergeron, *J. Chem. Educ.*, 1977, **54**, 204.
3 W. Saenger, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 344.
4 J. Szejtli, ed., 'Proc. Int. Symp. Cyclodextrins, 1st 1981,' Reidel, Dordrecht, 1982.
5 I. Tabushi, *Acc. Chem. Res.*, 1982, **15**, 66.
6 R. Breslow, *Science*, 1982, **218**, 532.
7 R. Breslow, *Chem. Br.*, 1983, **19**, 126.
8 P. A. Martic, S. E. Hartman, J. L. R. Williams, and S. Farid, in 'Solution Behavior of Surfactants,' eds. K. L. Mittal and E. J. Fendler, Plenum Press, New York, 1982, vol. 1, pp. 693—696.
9 W. G. Herkstroeter, P. A. Martic, S. E. Hartman, J. L. R. Williams, and S. Farid, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 2473.
10 W. G. Herkstroeter, *J. Polym. Sci., Polym. Chem. Ed.*, in the press.
11 S.-T. Cheung, M. A. Winnik, and A. E. C. Redpath, *Makromol. Chem.*, 1982, **183**, 1815.
12 R. B. Bauer, P. DeMayo, W. R. Ware, and K. C. Wu, *J. Phys. Chem.*, 1982, **86**, 3781.
13 T. Yorozu, M. Hoshino, and M. Immamuru, *J. Phys. Chem.*, 1982, **86**, 4426.
14 S. Hamai, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2721.
15 F. Cramer, W. J. Saenger, and H.-Ch. Spatz, *J. Am. Chem. Soc.*, 1967, **89**, 14.
16 K. Kano, I. Takenoshita, and T. Ogawa, *Chem. Lett.*, 1982, 321.
17 M. Otagiri, K. Uekama, and K. Ikeda, *Chem. Pharm. Bull.*, 1975, **23**, 188.
18 H. E. Edwards and J. K. Thomas, *Carbohydr. Res.*, 1978, **65**, 173.
19 A. Harada and S. Nozakura, *Polym. Bull.*, 1982, **8**, 141.
20 F. Cramer, *Chem. Ber.*, 1951, **84**, 851.
21 N. J. Turro, G. S. Cox, and X. Li, *Photochem. Photobiol.*, 1983, **37**, 149.
22 M. Masui, H. Sayo, and Y. Tsuda, *J. Chem. Soc. B*, 1968, 973.
23 C. K. Mann and K. K. Barnes, in 'Electrochemical Reactions in Nonaqueous Systems,' Marcel Dekker, New York, 1970, p. 87 and references therein.
24 D. Rehm and A. Weller, *Isr. J. Chem.*, 1971, **8**, 259.
25 W. R. Ware, *J. Phys. Chem.*, 1962, **66**, 455.
26 D. V. O'Connor, W. R. Ware, and J. C. Andre, *J. Phys. Chem.*, 1979, **83**, 1333.

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