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THE INCLUSION OF PYRONINE B AND PYRONINE Y BY BETA- AND GAMMA-CYCLODEXTRINS. A KINETIC AND EQUILIBRIUM STUDY.

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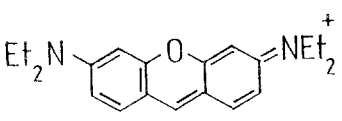
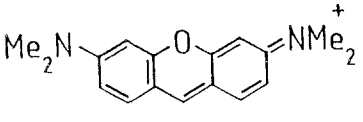
ABSTRACT. Equilibrium and temperature-jump spectrophotometric studies show that the mono-cation of pyronine B (PB) is included by beta- and gamma-cyclodextrins (βCD and γCD) to form the labile complexes PB.βCD, PB.γCD and $(PB)_2$.γCD in water. The equilibrium, kinetic and structural aspects of these complexes and those formed by pyronine Y are discussed in conjunction with data characterizing the inclusion of other dyes by cyclodextrins.

INTRODUCTION

The inclusion of organic dyes by cyclodextrins is a well known phenomenon, but the kinetics and mechanisms of such inclusion processes, particularly for the larger cyclodextrins, have not been much investigated.[1-4] In order to determine the effect of annular size on the dynamics of the inclusion process we have studied the inclusion of the mono-cations of pyronine B and pyronine Y (PB and PY):



PB



PY

by the beta- and gamma-cyclodextrins (βCD and γCD) which are α-1,4-linked cyclic heptamers and octamers of D-glucopyranose respectively characterized by internal annular diameters of 7-8 Å and 9-10 Å. The smaller αCD does not include PB and PY to a detectable extent.

RESULTS

All PB spectroscopic studies were carried out at pH 5.7 in aqueous 1.00 mol dm^{-3} NaCl at 298.2 K. The variation of the PB spectrum in the range 450-600 nm was consistent with the formation of a 1:1 inclusion complex only:

$$PB + \beta CD \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PB.\beta CD \qquad K_1 \qquad (1)$$

The variation of the relaxation time of this equilibrium, determined from temperature-jump studies at 555 nm, is given by:

$$1/\tau = k_1([PD] + [\beta CD]) + k_{-1} \qquad (2)$$

where all concentrations are equilibrium values existing prior to the temperature-jump. A linear regression of the variation of $1/\tau$ with total [βCD] in the range 10^{-4}-10^{-3} mol dm^{-3} yielded the parameters in Table 1.

A much larger variation of the PB spectrum was observed in the presence of γCD (Figure 1) consistent with the formation of both 1:1 and 2:1 inclusion complexes:

$$PB + \gamma CD \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PB.\gamma CD \qquad K_1 \qquad (3)$$

$$PB + PB.\gamma CD \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (PB)_2.\gamma CD \qquad K_2 \qquad (4)$$

Temperature-jump studies at 533 and 553 nm yielded the variation of the relaxation time (τ) with [γCD] shown in Figure 2. This variation is consistent with equilibrium (3) being particularly facile such that it is always at equilibrium while the less facile equilibrium (4), which incorporates the rate determining step for the processes producing the change in the spectrum, adjusts to the new temperature. (The temperature-jump was from 288.5 K to 298.2 K.) The variation of τ with [γCD] for this mechanism is given by eqn (5) in which all concentrations are the equilibrium values at 298.2 K.

$$1/\tau = \frac{k_2[PB]([PB.\gamma CD] + [PB] + 4[\gamma CD])}{([PB] + [\gamma CD] + 1/K_1)} + k_{-2} \qquad (5)$$

The inclusion of PY by γCD is characterized by spectral changes and τ variations consistent with equilibria analogous to (3) and (4), and a relaxation equation analogous to eqn (5). The derived parameters for both the PB/γCD and PY/γCD appear in Table 1 together with parameters from related systems.

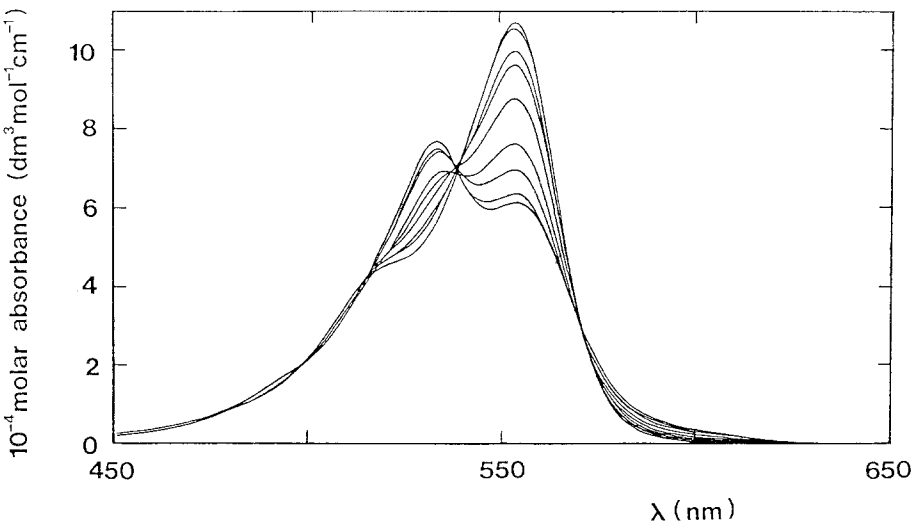


Figure 1. Variation of the PB spectrum in the presence of γCD at pH 5.70 in aqueous 1.00 mol dm^{-3} NaCl at 298.2 K. The molar absorbance at 550 nm decreases systematically as the total [γCD] increases sequentially from 0-4.093 × 10^{-3} mol dm^{-3}. Total [PB] = 9.7 × 10^{-6} mol dm^{-3}. These nine spectra exemplify the spectral variation observed for all thirty solutions studied.

Table 1. Dye-Cyclodextrin Inclusion Complex Equilibrium and Kinetic Parameters (298.2 K)

DYE	$K_1/10^2$ dm^3mol^{-1}	$K_2/10^5$ dm^3mol^{-1}	$k_2/10^9$ $dm^3mol^{-1}s^{-1}$	$k_{-2}/10^3$ s^{-1}
		γ-cyclodextrin		
pyronine B[a]	4.3±0.1	1.28±0.04	0.82±0.02	6.40±0.05
pyronine Y[a]	11.3±0.7	30±41	10±7	3.3±2.2
tropaeolin[b]	4.18±1.47	16.8±0.54	2.27±0.61	1.35±0.23
methyl orange[c]	0.45±0.07	20±11	9.4±5.1	4.8±0.8
crystal violet[d]	4.63±0.06	10.3±0.9	1.73±0.08	1.68±0.07
		β-cyclodextrin		
pyronine B[a]	73±31	-	-	-
($k_1/10^9$ = 0.11±0.01 $dm^3mol^{-1}s^{-1}$; $k_{-1}/10^3$ = 15±5 s^{-1})				
tropaeolin[b]	7.1±0.7	40±70	5±6	1.3±1.5

[a] This work [b] Ref. 4 [c] Ref. 2 [d] Ref. 3

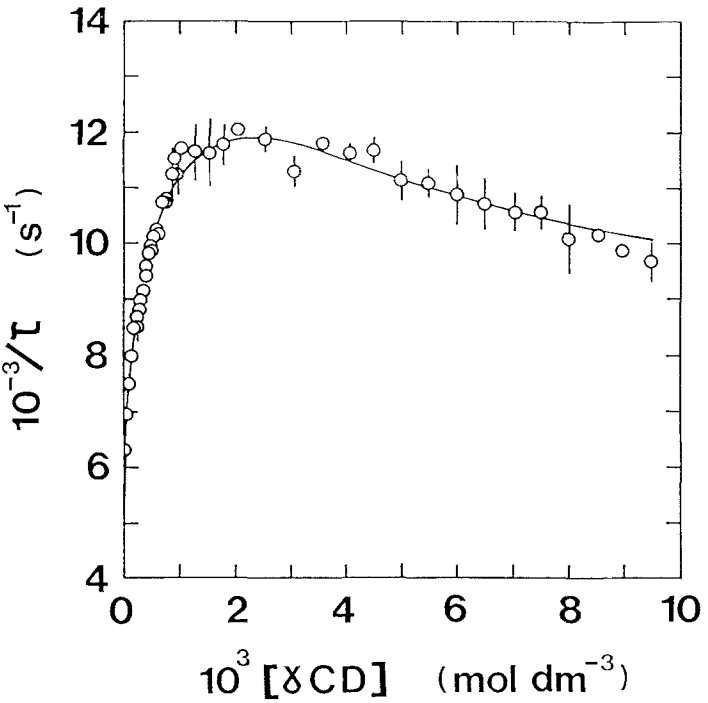


Figure 2. The variation of $1/\tau$ (298.2 K) for the PB/γCD system with the total [γCD]. Total [PB] varied in the range (9.1-9.8) × 10^{-6} mol dm^{-3}. The solid curve represents the best fit of the data to eqn (5).

DISCUSSION

The absence of detectable complex formation between PB and αCD, the formation of PB.βCD only, and the formation of PB.γCD and $(PB)_2$.γCD demonstrates the strong correlation between the size of the included dye and the annular diameters of αCD, βCD and γCD, which are 5-6 Å, 7-8 Å and 9-10 Å respectively. The replacement of the ethyl groups of PB by methyl groups in PY produces differences in K_1 and K_2 characterizing $(dye)_2$γCD (Table 1) indicating the influence of changes in dye structure on stabilities. A more substantial demonstration of this is afforded by the formation of $(tropaeolin)_2$βCD, which indicates that the nature of the dye is also important in determining the stoichiometry of the inclusion complex (Table 1).

The dimerization constant (K_d) for PB:

$$2PB \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (PB)_2 \qquad K_d \qquad (6)$$

was determined to be (1.3±0.5) × 10^3 dm^3mol^{-1}, and K_d = (1.1±0.2) × 10^3

dm^3mol^{-1} for PY under the same conditions as the cyclodextrin studies. Thus inclusion by γCD increases the stability of $(PB)_2$ and $(PY)_2$ by *ca* 100 and 3000 fold. The dimerization relaxation for both dyes occurred within the heating time of our temperature-jump equipment (*ca* 2 μs), and in consequence k_d and k_{-d} were not measurable. Similarly increases in the stability of $(dye)_2$ are observed for the other dyes in Table 1.

The variation of K_1, K_2, k_2 and k_{-2} for the dye/γCD systems (Table 1) is surprisingly small when the diversity of the nature of the five dyes studied is considered. (PB, PY and crystal violet exist as mono-cations under the conditions of study, whereas tropaeolin and methyl orange exist as mono-anions.) There are probably several factors determining these parameters, and fortuitous combinations of these factors may produce the small range of stability and rate constants. However it is possible that the dispersion force interactions between the dye monomers included $(dye)_2$, and between this dimer and the interior of the cyclodextrin annulus may be a dominant factor determining and constraining the magnitude range of the parameters characterizing $(dye)_2$γCD.

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