

Transport Method for Determining the Association Constants of Complexes Formed between Aromatic Hydrocarbons and α - and β -Cyclodextrin in Water

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Abstract. The association constants of 1 : 1 complexes formed in water between six aromatic hydrocarbons (*o*-, *m*-, and *p*-xylene, naphthalene, anthracene, and pyrene) and α - and β -cyclodextrin were determined by the transport method. The values are in good agreement with those determined by other methods.

Key words. Association constant, α -cyclodextrin complexes, β -cyclodextrin complexes, aromatic hydrocarbon complexes, transport method.

1. Introduction

The water-soluble doughnut-shaped α - and β -cyclodextrin (α - and β -CD) are macrocycles containing, respectively, six and seven α -(1,4)-linked D-glucopyranose units. They have been extensively studied in the last thirty years for their ability to include within their cavity a variety of organic and inorganic molecules and ions [1–3]. However, the association constants of the complexes formed between them and the aromatic hydrocarbons in water have been determined rather recently by several methods, such as the vaporization technique [4–6], fluorescence [7–9], and UV [7, 10] spectroscopy. There are two problems that may limit the accuracy of the methods used: (1) the low solubility of the aromatic hydrocarbons in water [9]; and (2) the significant adsorption of the aqueous aromatic hydrocarbons on the glass wall of the cell used [6, 8]. In this paper we report that the transport method [11], which avoids these two problems, is a better method for the determination of the association constants of the CD-aromatic hydrocarbon complexes.

2. Experimental Section

2.1. MATERIALS

All the the chemicals used were from commercial sources: α - and β -cyclodextrin (Sigma); *o*-, *m*-, and *p*-xylene (Merck); naphthalene, anthracene, and pyrene (Aldrich). The last three components were purified by recrystallization from ethanol and the others were used without any further purification.

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2.2. ULTRAVIOLET SPECTRA

UV spectra of the aromatic hydrocarbons were recorded using a Hitachi U-2000 spectrophotometer.

2.3. TRANSPORT EXPERIMENTS

These were carried out as described previously [11] at room temperature (27–29°C). However, besides performing each set of experiment at least twice, we also exchanged the role of the pair of U-tubes used (the ‘blank’ U-tube became the ‘sample’ U-tube and *vice versa*) and again measured the transport rates in duplicate. This additional step eliminated any error that might arise if the pair of U-tubes used were not exactly identical.

3. Method

We have shown earlier [11] that, for complexes of 1 : 1 host : guest stoichiometry, the association constant K_a defined in Equation 1 (where [HG], [H], and [G] denote, respectively, the concentrations in the aqueous phase of the complex, host, and guest) is related to the rates of transport of the aromatic hydrocarbon guest from one hexane phase to another through an aqueous phase. When $[HG] \gg [G]$ the relationship is given by Equation 2 (where r is the transport rate when the aqueous phase contains the host, r_0 the transport rate when no host is present, and M and M_0 denote the molecular masses of HG and G, respectively). When $[HG] \ll [G]$ the relationship is given by Equation 3 because the complexed guest is now essentially transported in its free form as the result of the dynamic equilibrium between the complexed and free guests. When $[HG] \simeq [G]$ the K_a value is

$$K_a = [HG]/[H][G] \quad (1)$$

$$K_a = \frac{1}{[H]} \left(\frac{r}{r_0} - 1 \right) \left(\frac{M}{M_0} \right)^{1/2} \quad (2)$$

$$K_a = \frac{1}{[H]} \left(\frac{r}{r_0} - 1 \right) \quad (3)$$

the average of the K_a values given by Equations 2 and 3 because the guest molecule is transported about equally in the free as well as the complexed form.

The transport rates of six aromatic hydrocarbons as guests (*o*-, *m*- and *p*-xylene, naphthalene, anthracene, and pyrene: the aromatic hydrocarbons chosen are those whose K_a values have been determined by other methods so that a comparison with our method can be made) from one hexane phase to another through an aqueous phase with and without α -CD and β -CD as host were measured using the U-tube method [11, 12]. The K_a values of the CD–aromatic hydrocarbon complexes were then calculated using the appropriate equations given above.

4. Results and Discussion

At a given wavelength the absorbance of the aromatic hydrocarbon in the receiving phase was plotted, using linear regression analysis, against the time taken by the

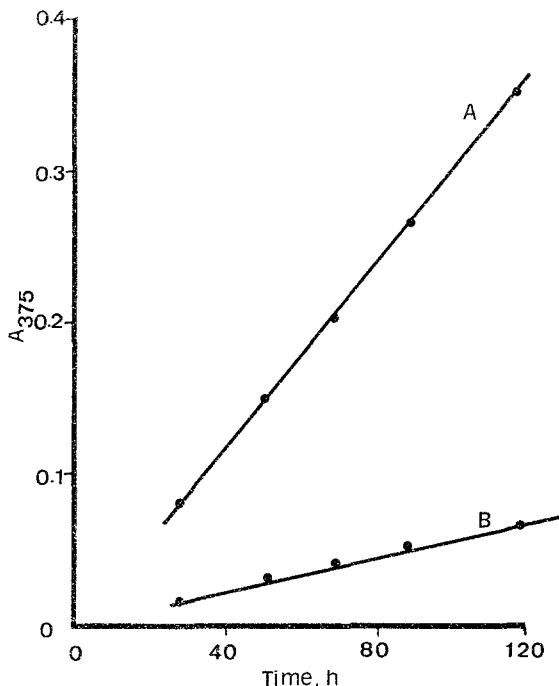


Fig. 1. Relationship between absorbance at 375 nm of anthracene in the receiving phase and time. The initial concentration of anthracene in the source phase is 3.0×10^{-3} M; (A) 3.0×10^{-3} M of β -CD in the aqueous phase and (B) no host in the aqueous phase; slope of line A is $2.95 \times 10^{-3} \text{ h}^{-1}(r)$ and line B $5.40 \times 10^{-4} \text{ h}^{-1}(r_0)$.

aromatic hydrocarbon to travel from the source phase to the receiving phase. The slope of the plot gives the transport rate [11, 12] (Figure 1 shows the plots for anthracene in the presence and absence of β -CD). The relative rates, r/r_0 , are given in Table I.

The ratios of $[\text{HG}]/[\text{G}]$ were calculated from the term $(r/r_0 - 1)$ (derived from Equations 1 and 3) and they fall into three distinct groups (Table II) namely; (1) $[\text{HG}] \ll [\text{G}]$ (Nos. 1–9), (2) $[\text{HG}] \gg [\text{G}]$ (No. 11): and (3) $[\text{HG}] \simeq [\text{G}]$ (Nos. 10, 12). The K_a values (Table II) of these three groups were calculated from Equations 3, Equation 2, and the average of Equations 2 and 3, respectively. Our K_a values for the xylenes and naphthalene as guests and α - and β -CD as hosts (Nos. 1–4, 7–10) are in good agreement with the literature values obtained by the vaporization and fluorescence methods. The value of 186 M^{-1} for the naphthalene- β -CD complex given by the UV method [10] seems low [4, 13]. In the case of anthracene and pyrene as guests, no literature K_a data are available for α -CD as host. Of the three reported K_a values for the pyrene- β -CD complex (No. 12), the two values obtained by the fluorescence method are not accurate (190 M^{-1} is a rough estimate [8] and 44 M^{-1} is the estimated lowest limiting value [9]). The value of 648 M^{-1} obtained by the UV method [10] is lower than our value of 910 M^{-1} . Our K_a value of 3870 M^{-1} for the anthracene- β -CD complex and that of 2300 M^{-1} obtained by the vaporization method [6] are of the same magnitude, but much higher than the

Table I. Association constants of 1:1 cyclodextrin:aromatic hydrocarbon complexes in aqueous solution at 27–29°C.

No.	Hydrocarbon	[G] ₀ ^a (M)	[H] ₀ ^b (M)	<i>r</i> / <i>r</i> ₀	(M/M ₀) ^{1/2}	<i>K</i> _a (M ⁻¹)	
						Eq. 2	Eq. 3
<i>Host = α-Cyclodextrin</i>							
1	<i>o</i> -Xylene	9.7 × 10 ⁻²	8.0 × 10 ⁻³	1.13	3.19	52 ± 13	16 ± 4
2	<i>m</i> -Xylene	9.7 × 10 ⁻²	6.0 × 10 ⁻³	1.19	3.19	101 ± 6	32 ± 2
3	<i>p</i> -Xylene	9.7 × 10 ⁻²	6.0 × 10 ⁻³	1.34	3.19	180 ± 70	56 ± 20
4	Naphthalene	5.0 × 10 ⁻⁴	7.5 × 10 ⁻³	1.58	2.93	227 ± 18	77 ± 6
5	Anthracene	3.0 × 10 ⁻³	3.0 × 10 ⁻³	1.05	2.54	43 ± 17	17 ± 7
6	Pyrene	2.0 × 10 ⁻³	3.0 × 10 ⁻³	1.08	2.41	64 ± 12	27 ± 5
<i>Host = β-Cyclodextrin</i>							
7	<i>o</i> -Xylene	6.5 × 10 ⁻²	1.0 × 10 ⁻³	1.21	3.42	718 ± 171	210 ± 50
8	<i>m</i> -Xylene	6.5 × 10 ⁻²	2.0 × 10 ⁻³	1.21	3.42	410 ± 171	120 ± 50
9	<i>p</i> -Xylene	6.5 × 10 ⁻²	1.0 × 10 ⁻³	1.23	3.42	787 ± 17	230 ± 5
10	Naphthalene	5.0 × 10 ⁻⁴	3.0 × 10 ⁻³	1.88	3.14	922 ± 188	294 ± 60
11	Anthracene	3.0 × 10 ⁻³	3.0 × 10 ⁻³	5.27	2.72	3870 ± 180	1423 ± 67
12	Pyrene	2.0 × 10 ⁻³	2.0 × 10 ⁻³	2.02	2.57	1311 ± 20	510 ± 8

^aInitial concentration of the aromatic hydrocarbon in the hexane source phase.

^bInitial concentration of the cyclodextrin host in the aqueous phase.

value of 420 M⁻¹ obtained by the UV method [10]. We believe the latter value is probably wrong (see below).

We reported earlier [14] that a linear relationship exists between log *K*_a and *N* (the number of aromatic rings in the guest molecules) when the host cavity is larger than the size of the aromatic hydrocarbon guests. For axial inclusions [10], CPK models indicate that the cavity of β-CD is large enough to accommodate the present aromatic hydrocarbons inside it (except pyrene). Therefore, we expect a linear relationship between log *K*_a and *N* for the β-CD complexes with xylenes, naphthalene, and anthracene as guests. Indeed a linear plot is observed (Figure 2, slope = 0.67, intercept = 1.53, correlation coefficient = 0.976, the log *K*_a value of 2.1 for benzene was taken from Ref. [5]). The point for pyrene deviates from the straight line, consistent with its size being greater than the β-CD cavity. A CPK model of the axial inclusion complex indicates that one aromatic ring of the pyrene guest can be completely enclosed within the β-CD cavity, while two other aromatic rings are partially enclosed. Thus, an equivalent of about two full aromatic rings of pyrene are enclosed in the β-CD cavity, consistent with the *K*_a value being close to that of the naphthalene-β-CD complex. If the literature *K*_a value of 420 M⁻¹ for anthracene is used instead of our value of 3870 M⁻¹, the point for anthracene deviates considerably from the straight line, indicating the former *K*_a value is too low. The slope of 0.67, significantly smaller than the values of 0.92 and 0.98 for cyclotetrachromotropyrene and cyclophane as hosts, respectively [14], is consistent with a less hydrophobic cavity in β-CD (the inside wall of the hydrophobic cavity is lined with seven ether oxygen atoms linking the seven D-glucopyranose units). No

Table II. Comparison of the association constants of 1 : 1 cyclodextrin : aromatic hydrocarbon complexes obtained by various methods.

No.	Hydrocarbon	[HG]/[G] ^a	K_a (M ⁻¹)	
			This work	Literature
<i>Host = α-Cyclodextrin</i>				
1	<i>o</i> -Xylene	0.13	16 ^b	22 ^e
2	<i>m</i> -Xylene	0.19	32 ^b	40 ^e
3	<i>p</i> -Xylene	0.34	56 ^b	72 ^e
4	Naphthalene	0.58	77 ^b	83 ^e
5	Anthracene	0.05	17 ^b	
6	Pyrene	0.08	27 ^b	
<i>Host = β-Cyclodextrin</i>				
7	<i>o</i> -Xylene	0.21	210 ^b	300 ^e
8	<i>m</i> -Xylene	0.21	120 ^b	160 ^e
9	<i>p</i> -Xylene	0.23	230 ^b	240 ^e
10	Naphthalene	0.88	608 ^c	630 ^g ; 685 ^f ; 850 ^g ; 186 ^h
11	Anthracene	4.27	3870 ^d	420 ^h ; 2300 ⁱ
12	Pyrene	1.02	910 ^c	648 ^h ; 190 ^j ; 44 ^k

^aCalculated from $(r/r_0 - 1)$.

^bFrom Equation 3 (Table I).

^cAverage of the K_a values obtained from Equations 2 and 3 (Table I).

^dFrom Equation 2 (Table I).

^eRef. [5], vaporization method.

^fRef. [7], fluorescence method.

^gRef. [9], fluorescence method.

^hRef. [10], UV method.

ⁱRef. [6], vaporization method.

^jRef. [8], rough estimate by fluorescence method.

^kRef. [9], lowest limiting value estimated by fluorescence method.

linear relationship between $\log K_a$ and N is observed in the case of α -CD as host because its cavity is smaller than the aromatic hydrocarbon guests (except *p*-xylene, which can penetrate axially).

5. Conclusion

The transport method is a better method for the measurement of the association constants of 1 : 1 complexes formed between aromatic hydrocarbons and α - and β -cyclodextrin in an aqueous medium.

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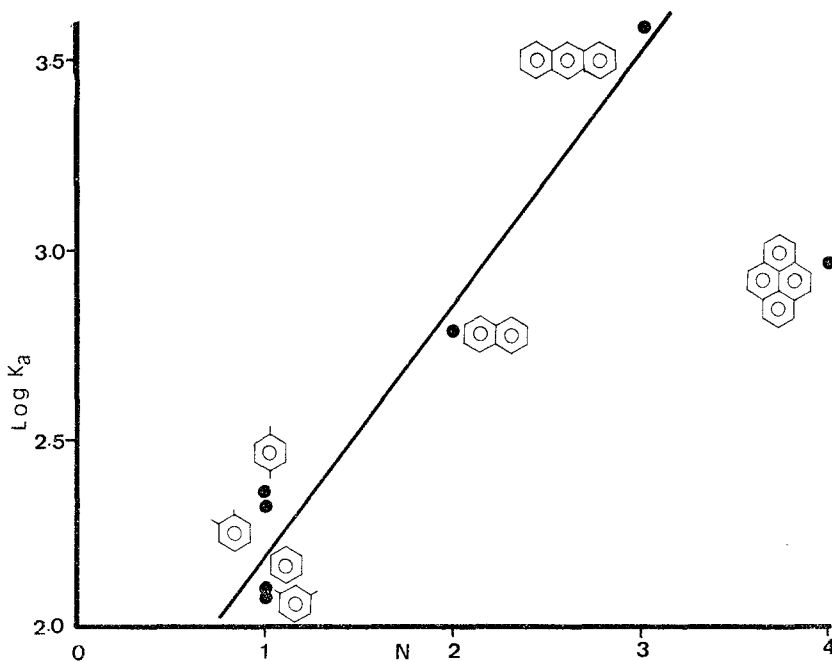


Fig. 2. Relationship between $\log K_a$ and the number of aromatic rings (N) in the hydrocarbon guests; host is β -CD.

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