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Transport Method for Determining the Stability Constants of Complexes with Cyclodextrins (α-, β- and γ-) and Starch as Hosts, Molecular Iodine and Triiodide Anion as Guests in Water

Yeh bo leng
BO-LONG POH* and CHIN LING LOH

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

ABSTRACT

A transport method was introduced to determine the stability constants of the 1:1 complexes formed between cyclodextrins (α-, β- and γ-) as hosts and molecular iodine and triiodide anion as guests in an aqueous medium. The stability constants obtained when the guest is iodine are 3.7×10^3, 2.4×10^2 and 1.4×10^2 M^{-1} at 27 °C for α-, β- and γ-cyclodextrin respectively. When the guest is triiodide anion, the stability constants obtained are 4.1×10^3, 7.2×10^2 and 2.2×10^2 M^{-1} respectively for α-, β- and γ-cyclodextrin. No complexation between starch and iodine was observed. However, the starch molecule was induced into a folded conformation resembling β-cyclodextrin to complex wth triiodide anion, with a stability constant of 7.9×10^2 M^{-1}.

Key words: cyclodextrin-iodine complex, cyclodextrin-triiodide anion complex, starch-triiodide anion complex, stability constant, transport method

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1. INTRODUCTION

Cyclodextrins (α-, β- and γ-) form complexes with both molecular iodine and triiodide anion and they are good models for the starch-iodine complex. The complexes formed in an aqueous medium are of 1:1 host to guest stoichiometry [1,2]. Their stability constants have been determined by spectrophotometric [1], potentiometric [3], solubility [4] and volatization [5] methods.

In this paper, we introduce a transport method of determining the stability constants of these complexes and use it to gain an understanding of the conformation of the starch-iodine complex.

2. EXPERIMENTAL

2.1 Materials

α-, β- and γ-cyclodextrin (Sigma), iodine, potassium iodide and starch (Fisher) were commercial samples.

2.2 Visible spectra

Visible spectra of iodine in *n*-hexane solution were recorded with a Hitachi U-2000 spectrophotometer. The absorbance maximum at 522 nm (ε 915) was used for quantitative determination of iodine.

2.3 Transport method

Transport experiments were carried out at room temperature (27 ± 1 °C) using the U-tube (Figure 1) described by Diederich and Dick [6,7]. A 16 mL aqueous solution of the host (1.0×10^{-3} to 2.0×10^{-3} M for the cyclodextrins and 0.8 to 2.8 g/L for starch) was placed at the bottom of the U-tube. For experiments carried out in the presence of iodide anion, 1.0×10^{-2} M of potassium iodide was added to the aqueous phase. Atop this aqueous phase in one arm of the tube was placed 8 mL of *n*-hexane containing iodine (1.0×10^{-3} M) as the source phase. In the other arm 8 mL of *n*-hexane was placed atop the aqueous phase as the receiving phase. The aqueous phase was stirred with a small magnetic bar at a constant speed. An identical experiment, but without the host, was used as the blank. Samples of 2.5 mL were taken from both the source and receiving phases (uniform in concentration) at regular time intervals of about four hours or more for the quantitative determination of iodine in these two phases using the visible absorbance at 522 nm. After each determination (less than a minute taken) the sample was returned to the two arms of the U-tube. No significant error due to sampling was observed. For each host, experiments were carried out with four different host concentrations and in duplicates. There was negligible hydrolysis of iodine to iodide anion in the aqueous phase in the duration of the experiments, consistent with the reported small iodine hydrolysis equilibrium constant [8]. A representative sample of the raw data obtained is shown in Table 1.

2.4 Stability constants

For the complexation of iodine in the aqueous phase of the U-tube, the stability constant K_1 of the 1:1 host (H) to guest (I_2) complex ($H.I_2$) is given by Equation (1).

$$K_1 = [H.I_2]/[H][I_2] \qquad (1)$$

Using the assumption that the rate of diffusion of iodine from the hexane source phase into the aqueous phase containing the host is the sum of the iodine diffusion rate for the blank and that caused by complexation with the host [7], the term $[I_2]$ is equal to the concentration of iodine in the aqueous phase of the blank U-tube and calculated by Equation (2).

$$[I_2] = \{[I_2]_O - [I_2]_S - [I_2]_R\}_B/2 \qquad (2)$$

The three terms $[I_2]_O$, $[I_2]_S$ and $[I_2]_R$ refer to the initial concentration of iodine in the source phase, the concentration of iodine in the source phase at time t and the concentration of iodine in the receiving phase at time t respectively. The subscript B refers to the blank U-tube. The dilution factor 2 takes into account the volume of the aqueous phase is twice that of the source and receiving phase.

The term $[H.I_2]$ is calculated from Equation (3) where $[I_2]_H$ (the subscript H refers to the host U-tube) is obtained from the U-tube containing the host using Equation (4) which is analogous to Equation (2).

$$[H.I_2] = [I_2]_H - [I_2] \qquad (3)$$

$$[I_2]_H = \{[I_2]_O - [I_2]_S - [I_2]_R\}_H/2 \qquad (4)$$

The term [H] is calculated from Equation (5) where $[H]_O$ refers to the initial concentration of the host.

$$[H] = [H]_O - [H.I_2] \qquad (5)$$

A representative example showing the calculations of K_1 using Equation (1) for α-cyclodextrin as host is shown in Table 2.

When triiodide anion is the guest, the stability constant K_2 for the 1:1 complex is given by Equation (6).

$$K_2 = [H.I_3^-]/[H][I_3^-] \qquad (6)$$

Under the present experimental conditions, any iodine molecule from the hexane source phase that gets into the aqueous phase is practically converted to the triiodide anion by the iodide anion present in the aqueous phase since the equilibrium constant between iodine and triiodide anion is about 700 M^{-1} [4]. Therefore, replacing $[I_2]$ with $[I_3^-]$ and $[I_2]_H$ with $[I_3^-]_H$ in all the above equations for the case of iodine as guest we can obtain $[H.I_3^-]$ and calculate K_2. A representative example showing the calculations of K_2 for α-cyclodextrin as host is shown in Table 3.

3 RESULTS AND DISCUSSION

3.1 Complexation with iodine

Figure 2 is a plot of the absorbance of iodine in the hexane source phase (with a host in the aqueous phase) against the absorbance of iodine in the hexane source phase for the blank, taken at various time intervals. A host that can complex with iodine in the aqueous phase induces a faster flow of iodine from the hexane source phase to the aqueous phase, resulting in a larger decrease in the iodine absorbance. Figure 2 shows that all the three cyclodextrins complex with iodine, the strongest complexation is with α-cyclodextrin and the weakest complexation with γ-cyclodextrin. Starch does not have any noticeable complexation with iodine, as its plot falls on the line with no complexation (the dotted line of unit slope) and the characteristic blue color for the starch-iodine complex was not observed in the aqueous phase. The absence of any starch-iodine complexation in the absence of iodide anion is consistent with earlier reports [1,9].

The values of the stability constant K_1 of the 1:1 cyclodextrin-iodine complexes (Table 4) obtained from Equation (1) are of the same magnitude as those obtained by other methods, thus giving a strong support to the validity of our method.

3.2 Complexation with triiodide anion

Figure 3 is a plot of the absorbance of iodine in the hexane source phase (with a host and potassium iodide in the aqueous phase) against the absorbance of iodine in the hexane source phase for the blank (containing only potassium iodide in the aqueous phase), taken at various time intervals. The three cyclodextrins as well as starch complex with the triiodide anion (the dotted line of unit slope is for no complexation). The plot for starch falls between the plots for α- and β-cyclodextrin, indicating the cavity size of the induced folded conformation of starch enclosing the triiodide anion is bigger than that of α-cyclodextrin but smaller than that of β-cyclodextrin. For such a size, CPK molecular models indicate that the folded conformation of starch consists of seven glucose units, not all lying on the same plane.

Thoma and French [1] as well as Diard and coworkers [3] reported that α-cyclodextrin binds with triiodide anion rather than iodide anion whereas Sano and coworkers [10] reported the reverse. Our results shown in Figure 3 support the former. Preferential complexation with triiodide anion results in a larger decrease of iodine in the hexane source phase compared with the blank, as observed in Figure 3, whereas preferential complexation with iodide anion does not since iodide anion is already present in large excess in the aqueous phase.

The values of the stability constant K_2 of the 1:1 cyclodextrin-triiodide anion complexes (Table 5) were obtained from Equation (6). Treating the starch molecule as a series of β-cyclodextrin to obtain [H] for starch, the K_2 value of $7.9 \times 10^2 M^{-1}$ was similarly obtained for the starch-triiodide anion complex. The K_2 values are lower, especially that of α-cyclodextrin as host, than those reported in the literature [3].

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TABLE 1. Variation of iodine concentrations in the hexane source and receiving phases with time

Time (hour)	Sample[a]		Blank	
	Source phase, M	Receiving phase, M	Source phase, M	Receiving phase, M
0	1.016×10^{-3}	0	1.016×10^{-3}	0
3.8	8.478×10^{-4}	0	9.909×10^{-4}	0
8.3	7.451×10^{-4}	1.857×10^{-5}	9.822×10^{-4}	5.462×10^{-6}
22.5	5.714×10^{-4}	5.681×10^{-5}	9.516×10^{-4}	1.966×10^{-5}
26.4	5.353×10^{-4}	6.883×10^{-5}	9.406×10^{-4}	2.294×10^{-5}
31.8	5.047×10^{-4}	9.177×10^{-5}	9.341×10^{-4}	3.059×10^{-5}
56.5	4.239×10^{-4}	1.453×10^{-4}	9.035×10^{-4}	5.135×10^{-5}
79.3	3.769×10^{-4}	1.912×10^{-4}	8.784×10^{-4}	7.757×10^{-5}

[a] 2.00×10^{-3} M of α-cyclodextrin as host in the aqueous phase.

TABLE 2. Calculations of K_1 using Equation (1) for the 1:1 α-cyclodextrin-I_2 complex[a]

Time (h)	$[I_2]$, M	$[H.I_2]$, M	[H], M	K_1, M^{-1}
3.8	1.26×10^{-5}	7.15×10^{-5}	1.93×10^{-3}	2.9×10^{3}
8.3	1.42×10^{-5}	1.12×10^{-4}	1.89×10^{-3}	4.2×10^{3}
22.5	2.24×10^{-5}	1.72×10^{-4}	1.83×10^{-3}	4.2×10^{3}
26.4	2.62×10^{-5}	1.80×10^{-4}	1.82×10^{-3}	3.8×10^{3}
31.8	2.57×10^{-5}	1.84×10^{-4}	1.81×10^{-3}	3.9×10^{3}
56.5	3.06×10^{-5}	1.93×10^{-4}	1.81×10^{-3}	3.5×10^{3}
79.3	3.00×10^{-5}	1.94×10^{-4}	1.81×10^{-3}	3.6×10^{3}
			Average K_1	$(3.7 \pm 0.4) \times 10^{3}$

[a] Initial concentrations of iodine in the source hexane phase and α-cyclodextrin in the aqueous phase are 1.02×10^{-3} and 2.00×10^{-3} M respectively.

TABLE 3. Calculations of K_2 using Equation (6) for the 1:1 α-cyclodextrin-I_3^- complex[a]

Time (h)	$[I_3^-]$, M	$[H.I_3^-]$, M	[H], M	K_2, M^{-1}
0.6	1.86×10^{-5}	1.15×10^{-4}	1.65×10^{-3}	3.7×10^{3}
1.5	3.50×10^{-5}	2.30×10^{-4}	1.54×10^{-3}	4.3×10^{3}
2.7	5.35×10^{-5}	3.48×10^{-4}	1.42×10^{-3}	4.6×10^{3}
3.8	6.61×10^{-5}	3.88×10^{-4}	1.38×10^{-3}	4.3×10^{3}
5.6	7.81×10^{-5}	4.13×10^{-4}	1.36×10^{-3}	3.9×10^{3}
9.2	8.58×10^{-5}	4.14×10^{-4}	1.36×10^{-3}	3.6×10^{3}
33.9	7.27×10^{-5}	4.24×10^{-4}	1.35×10^{-3}	4.3×10^{3}
			Average K_2	$(4.1 \pm 0.3) \times 10^{3}$

[a] Initial concentrations of iodine in the source hexane phase and α-cyclodextrin and potassium iodide in the aqueous phase are 1.02×10^{-3} , 2.00×10^{-3} and 1.04×10^{-2} M respectively.

TABLE 4. Stability constant K_I of 1:1 complexes formed between iodine and α-, β- and γ-cyclodextrin in water

Cyclodextrin	K_I, M^{-1} (This work)[a]	K_I, M^{-1} [refs.3,5][b]
α	$(3.7 \pm 0.4) \times 10^3$	1.5×10^4; 2×10^4; 2×10^3; 8.3×10^3; 9.4×10^3
β	$(2.4 \pm 0.2) \times 10^2$	1.0×10^2; 1.5×10^2; 1.9×10^3
γ	$(1.4 \pm 0.2) \times 10^2$	13; 24; 3.5×10^2

[a] at 27 °C; [b] at 25 °C

TABLE 5. Stability constant K_2 of 1:1 complexes formed between triiodide anion and α-, β- and γ-cyclodextrin and starch in water

Host	K_2, M^{-1} (This work)[a]	K_2, M^{-1} [ref.3][b]
α- cyclodextrin	$(4.1 \pm 0.3) \times 10^3$	2.3×10^5; 3.3×10^5
β- cyclodextrin	$(7.2 \pm 0.5) \times 10^2$	1.9×10^3; 2.2×10^3; 5.0×10^3
γ- cyclodextrin	$(2.2 \pm 0.2) \times 10^2$	5.0×10^2
Starch[c]	$(7.9 \pm 0.5) \times 10^2$	

[a] at 27 °C; [b] at 25 °C

[c] Starch treated as a chain of β-cyclodextrin molecules.

Figure captions

Figure 1. U-tube for transport experiment.

Figure 2. Absorbance at 522 nm of iodine in the hexane source phase at various time intervals at 27 °C (x-axis for the blank and y-axis for in the presence of hosts); $[I_2]_O = 1.05 \times 10^{-3}$ M and $[H]_O = 2.00 \times 10^{-3}$ M for α-, β- and γ-cyclodextrin, and 1.42 g/L for starch.

Figure 3. Absorbance at 522 nm of iodine in the hexane source phase at various time intervals at 27 °C (x-axis for the blank and y-axis for in the presence of hosts); $[I_2]_O = 1.00 \times 10^{-3}$ M, [KI] = 1.00×10^{-2} M and $[H]_O = 1.00 \times 10^{-3}$ M for α-, β- and γ-cyclodextrin, and 0.83 g/L for starch.

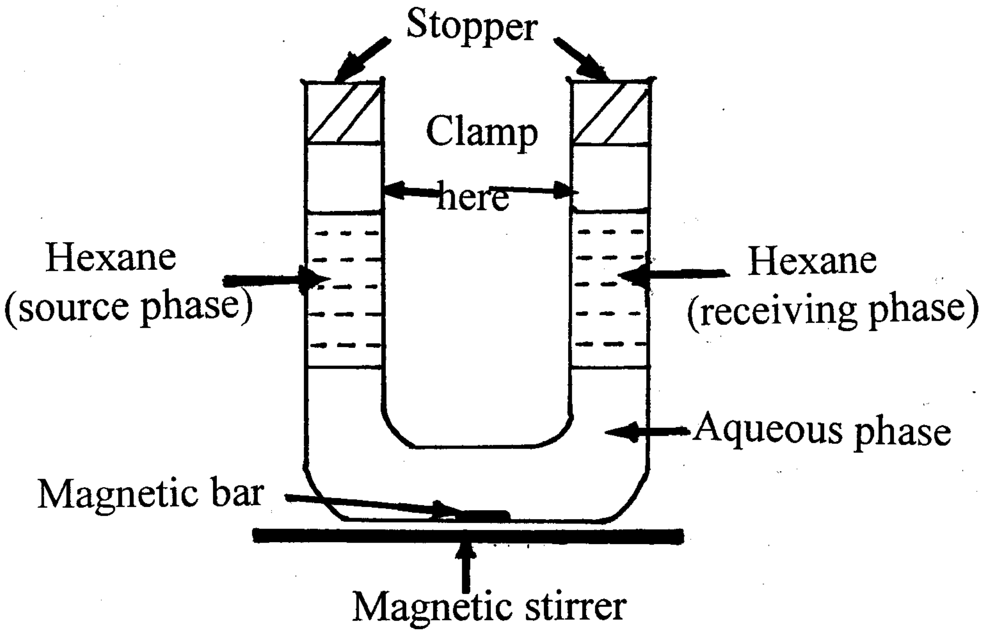
Stopper
Clamp here
Hexane (source phase)
Hexane (receiving phase)
Aqueous phase
Magnetic bar
Magnetic stirrer

Fig 1 PoH

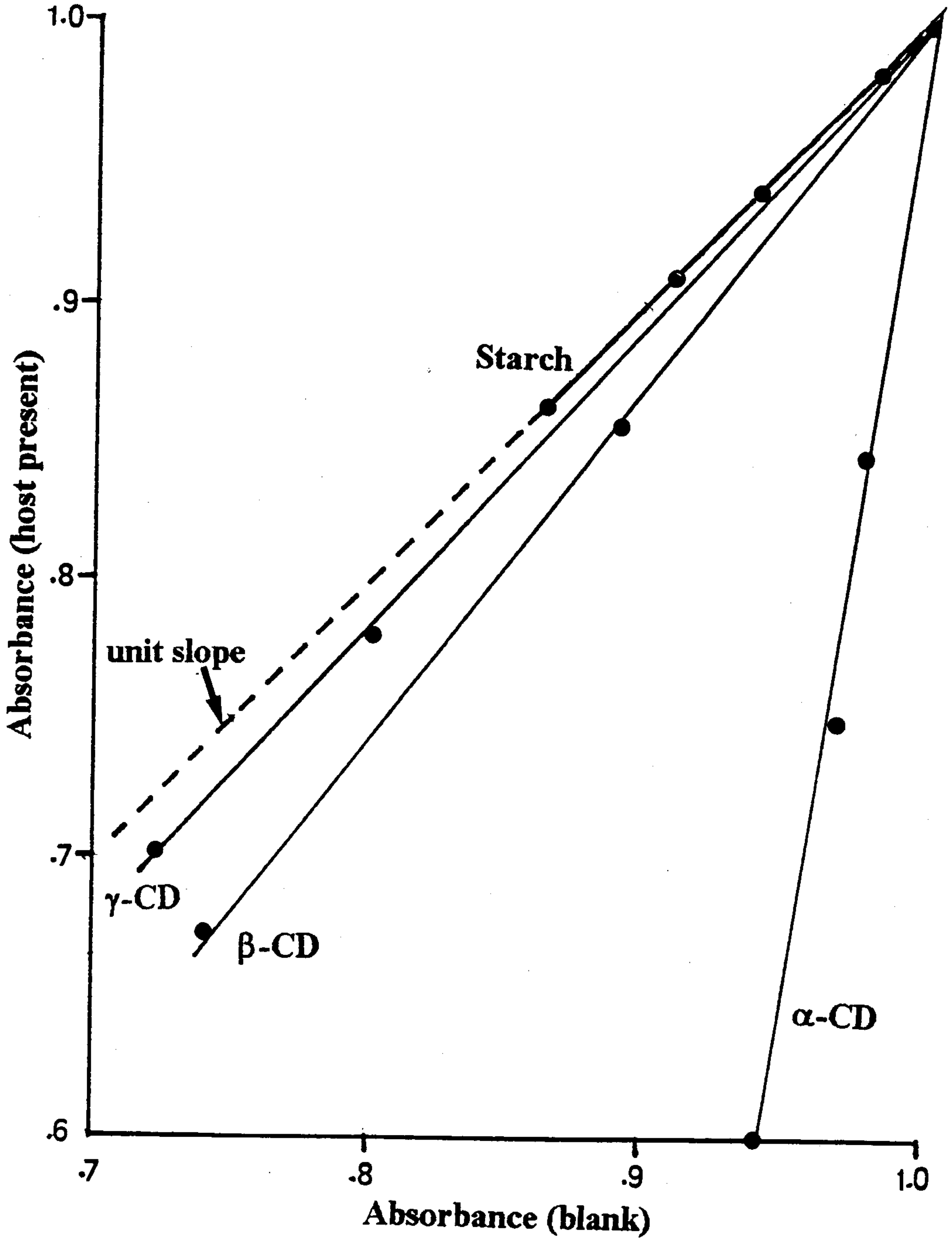
1.0
.9
.8
.7
.6
Absorbance (host present)
Starch
unit slope
γ-CD
β-CD
α-CD
.7
.8
.9
1.0
Absorbance (blank)

Fig 2 PoH

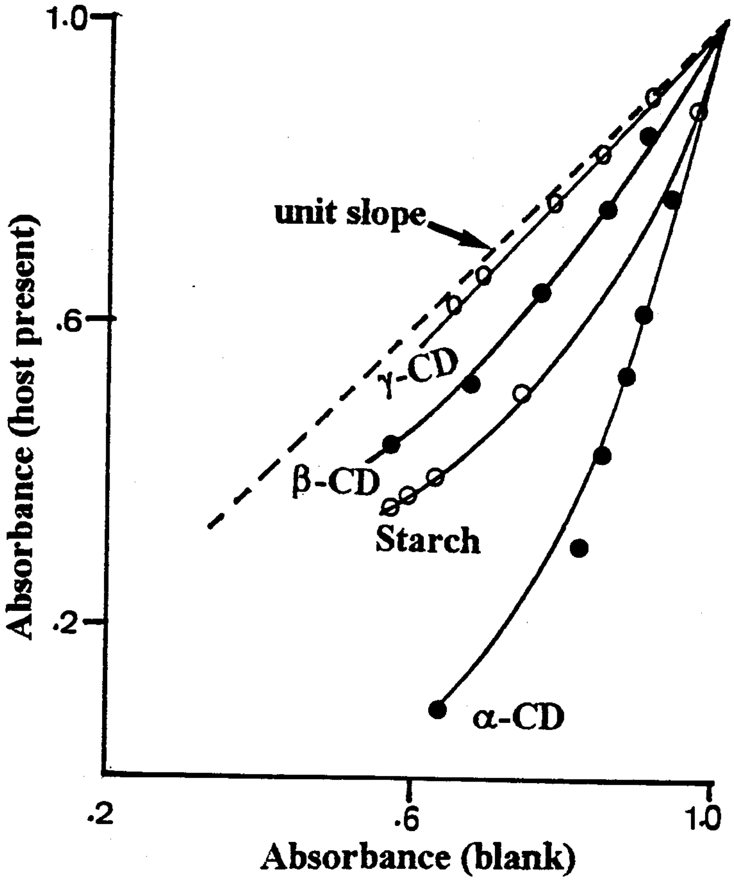
1.0
.6
.2
Absorbance (host present)
unit slope
γ-CD
β-CD
Starch
α-CD
.2
.6
1.0
Absorbance (blank)

Fig 3 PoH