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Coprecipitation of Aromatic Hydrocarbons from Water with β -Cyclodextrin

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Cyclodextrins (CyDs) are cyclic oligosaccharides comprising six, seven, or eight glucopyranose units (called α , β , or γ , respectively) with a central cavity of the corresponding size. It is well-established that CyDs form inclusion complexes with a variety of molecular species (guests) in an aqueous medium. In complexation, both the size (and shape) and hydrophobicity of a guest molecule play important roles.

In analytical chemistry, CyDs have been used as modifiers^{1,2} in the solvent extraction or carriers³ which selectively transport certain isomers. We recently found that β -CyD is easily precipitated from aqueous solution upon introducing a cyclohexane vapor into the solution. There is a possibility that, when hydrophobic solutes are present in the aqueous solution, these solutes could be coprecipitated with CyD.

Experimental

Reagents

All of the reagents used were of analytical reagent grade. Deionized distilled water was used throughout the experiments. Stock solutions of aromatic hydrocarbons were prepared by adding a known amount of each hydrocarbon into chloroform. Working solutions were prepared by suitable dilution with chloroform. An appropriate amount of β -CyD (Nakarai Chemical Co.), dried over phosphorus pentoxide under vacuum, was weighed and dissolved in water in order to prepare CyD solutions of the desired concentrations.

Apparatus and procedure

The device used to precipitate β -CyD from a sample solution was the same as that mentioned in a previous paper;⁴ Teflon film and a trap were removed from the device for the present use.

A 50 cm³ portion of the β -CyD solution was placed in a cylindrical separatory funnel (6.5 cm i.d., 600 cm³ capacity), and a 0.1 cm³ portion of the working chloroform solution of the sample hydrocarbon was added to the CyD solution; the mixture was gently hand-shaken in the funnel. The CyD did not precipitate in

this stage and there was no appearance of chloroform in the liquid phase (chloroform dissolves 0.82 g in 100 g water at 25°C). A 10 cm³ portion of cyclohexane was placed in a test-tube (2.8 cm i.d.×25 cm). The funnel and the test-tube were connected together with a Viton diaphragm air pump (Iwaki Co., AP-032Z). The cyclohexane vapor generated by bubbling air was dispersed through the aqueous sample solution *via* a sintered glass ball and circulated in the closed system; the flow rate of air pump was set at 100 to 500 cm³/min. The aqueous solution becomes turbid owing to CyD precipitation just after the introduction of cyclohexane vapor.

Vapor-circulation was continued for two minutes, and a 5 cm³ portion of the turbid solution was immediately removed from the funnel and diluted with water to 75 cm³. The suspension of CyD became clear due to this dilution. A 5 cm³ portion of cyclohexane was added to the solution; CyD does not precipitate in this step unless the CyD concentration of the aqueous sample solution is not very high. The sample hydrocarbon extracted with cyclohexane was measured in the way that will be described shortly afterward. The amount of the hydrocarbon found in the turbid solution of 5 cm³ was multiplied by 10, and the total recovery in percent was calculated by referring to the sample hydrocarbon initially taken.

The remainder of the turbid solution (45 cm³) was withdrawn from the funnel, transferred into a centrifuge tube, and centrifuged for 10 min at 4500 rpm. A 15 cm³ portion of the supernatant solution was diluted with water to 75 cm³ and extracted with cyclohexane (5 cm³). The amount of the hydrocarbon remaining in the aqueous phase through the CyD precipitation procedure was determined and the residual percent was estimated.

To the solid phase deposited on the centrifuge tube was added successively a suitable portion of water to dissolve the CyD. The aqueous solution was diluted to a certain volume of 100 to 500 cm³, depending on the detector sensitivity and on the CyD collecting ability for the hydrocarbon of interest. A 25 cm³ portion of the aqueous solution was diluted with water to 75 cm³ and extracted with cyclohexane (5 cm³). The amount of the

Table 1 Experimental conditions and results

Hydrocarbon	Concentration of hydrocarbon in β -CyD solution ^a / mol dm ⁻³	Wavelength/nm			Recovery, %			Complex formation constant ^e / dm ³ mol ⁻¹
		UV absorption	Fluorescence		Suspension ^b	Supernatant ^c	β -CyD solid phase ^d	
			Ex.	Em.				
Anthracene	1.0×10 ⁻⁷ (2.2×10 ⁻⁷)		253	378	95	10	87	3000
Biphenyl	2.0×10 ⁻⁵ (7.0×10 ⁻⁴)	247			76	10	61	2600
Phenanthrene	1.5×10 ⁻⁶ (6.5×10 ⁻⁶)		252	365.5	100	3	98	1500
Fluorene	1.0×10 ⁻⁵ (1.0×10 ⁻⁵)	261			89	2	87	1490
Naphthalene	4.0×10 ⁻⁶ (2.4×10 ⁻⁴)	220.4			83	5	74	900
Fluoranthene	4.0×10 ⁻⁷ (1.0×10 ⁻⁶)		360	462	89	3	87	160
Pyrene	2.0×10 ⁻⁷ (5.7×10 ⁻⁷)		335.5	383.5	101	3	89	160

a. Concentration of β -CyD in aqueous sample solutions: 3.0×10⁻³ mol dm⁻³. The value given in the parentheses is the solubility of the hydrocarbon in water. b. Total recovery. c. Residual percent. d. Coprecipitation percent. e. The 1:1 complex formation constant taken from ref. 6.

hydrocarbon coprecipitated with CyD was determined and the coprecipitation percent was estimated.

Spectrophotometric or spectrofluorometric measurements were made on the cyclohexane extracts. Calibration graphs were prepared for each hydrocarbon by shaking 75 cm³ water with 5 cm³ cyclohexane solutions of hydrocarbon of known concentration; it had been confirmed in the preliminary experiment that the extractability of hydrocarbon was not appreciably affected by the presence of CyD in the aqueous phase at the concentrations employed. The wavelengths selected for the hydrocarbon are listed in Table 1, where the concentration of hydrocarbon in the sample aqueous solution of 50 cm³ and the aqueous solubility of the hydrocarbon are also listed. Runs were made under the condition that the hydrocarbon concentration in each sample aqueous solution was lower than the hydrocarbon solubility in water.

Results and Discussion

The total recovery in percent, the residual percent, and the coprecipitation percent for the hydrocarbons studied are shown in Table 1. The total recovery is not necessarily equal to 100%. During cyclohexane vapor circulation, volatile hydrocarbons, such as biphenyl and probably naphthalene, are vaporized to some extent from the aqueous CyD solution and transferred into the cyclohexane reservoir. Benzene, the most volatile aromatic hydrocarbon, was recovered only 0.2% from the β -CyD solid phase, 5% from the suspension, and 2% from the supernatant (the total recovery amounts to only 7.2%). Since the hydrocarbons studied in this work exhibit more or less volatility, long-time aeration is undesirable (two-minute-aeration is satisfactory). When the volume of an aqueous sample solution was increased from 50 cm³ to 200 cm³, it was necessary to circulate cyclohexane vapor for 5 min to make the

solution turbid.

Using anthracene as a test hydrocarbon, runs were made at β -CyD concentrations of (1.5, 2.0, 2.5, 3.0, and 4.0)×10⁻³ mol dm⁻³. The coprecipitation percent at 1.5×10⁻³ mol dm⁻³ was found to be *ca.* 17% lower than that obtained at (3.0 and 4.0)×10⁻³ mol dm⁻³ (both gave the same coprecipitation percent).

It was found that much higher concentrations are necessary to precipitate α - or γ -CyD from water. This is probably due to either or both of the following reasons: (1) the much higher solubility of these two hosts in water; the solubilities at 25°C are 14.5(α), 1.85(β), and 23.2 g(γ) in 100 g water, and (2) the much lower complex formation constant of the two hosts with cyclohexane⁵ (the 1:1 formation constant is 9 (α), 156 (β), and 11 dm³ mol⁻¹(γ)). Using sample solutions with high CyD concentration, the solid phase that is precipitated increases to a large mass, making subsequent treatments difficult.

The precipitation mechanism of the CyD dissolved in water was not studied in this work. There are two possible causes: one is a change in the polarity of the aqueous phase; the other is the formation of an inclusion complex with cyclohexane. Let us consider the latter case:



and



Upon cyclohexane vapor being introduced, the aqueous sample solution is then saturated with cyclohexane; its concentration remains constant during the vapor circulation, with a cyclohexane solubility of 6.9×10⁻⁴ mol dm⁻³ at 25°C. By considering the complex formation constant of Eq. (1), it can be seen that *ca.* 90% of the β -CyD is present in the free uncomplexed form when the concentration of β -CyD is set at 3.0×10⁻³ mol dm⁻³. If,

however, β -CyD precipitates *via* Eq. (2), β -CyD in the free form is assumed to become reduced to 22% as a result of the following experiment. The β -CyD precipitated from its $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous solution was collected after circulating cyclohexane vapor for 2 min, dried at 110°C and then over P_2O_5 at room temperature under vacuum, and weighed; *ca.* 76% of β -CyD was recovered in the solid form from the aqueous solution in the absence of sample hydrocarbon.

As a measure of the stability of the inclusion complex, we take the 1:1 complex formation constant of the hydrocarbon with β -CyD listed in Table 1. No positive correlation was observed between the coprecipitation percent and the formation constant, indicating that the hydrocarbon is coprecipitated with CyD without being included in its cavity. Let us consider the case in which biphenyl and cyclohexane are in equilibrium with β -CyD just before CyD precipitation occurs. Then, the equilibrium concentration of $\beta\text{-CyD} \cdot \text{C}_6\text{H}_{12}$ and that of $\beta\text{-CyD} \cdot \text{C}_{12}\text{H}_{10}$ is estimated to be $(0.29 \text{ and } 0.017) \times 10^{-3} \text{ mol dm}^{-3}$, respectively, when the initial concentration of β -CyD is set at $3.0 \times 10^{-3} \text{ mol dm}^{-3}$. Even though biphenyl may be present partly as $\beta\text{-CyD} \cdot \text{C}_{12}\text{H}_{10}(\text{s})$, the amount seems to be extremely small. Cyclohexane in a sample aqueous solution, the concentration of which is maintained by continuous vapor circulation at a relatively high level (almost equal to its aqueous solubility) predominates Eq. (2). Therefore, biphenyl, once precipitated as the inclusion complex, may be easily dissociated.

If it is true that the hydrocarbon is coprecipitated with β -CyD without forming an inclusion complex, the use of non-cyclic saccharides may be effective. We thus used dextran $((\text{C}_6\text{H}_{10}\text{O}_5)_n, \text{M.W.}=60000-90000 \text{ and } 100000-200000)$ and dextrin $((\text{C}_6\text{H}_{10}\text{O}_5)_n \cdot x\text{H}_2\text{O})$. These saccharides, however, cannot be precipitated from an aqueous solution, even at nearly saturated concentra-

tions, by the introduction of cyclohexane vapor.

In conclusion, this work was initiated while hoping that hydrophobic aromatic hydrocarbons would be coprecipitated with β -CyD by forming inclusion complexes. The coprecipitation percent, however, was found not to be related to the inclusion complex formation constant of the hydrocarbon with β -CyD. Although the coprecipitation mechanism is still not clear, the method proposed here is useful for collecting low volatile aromatic hydrocarbons from water to the solid β -CyD phase.

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