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Isomer Compositions of Trimethyl- or Trichlorobenzenes in α-Cyclodextrin Precipitates Formed in an Aqueous Medium

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Upon introducing the vapor of binary mixtures of trimethylbenzene (TMB) or trichlorobenzene (TCB) isomers into an α-cyclodextrin (α-CyD) aqueous solution, and circulating it in a closed system, CyD was precipitated with the isomers. In (1,3,5–1,2,3 or 1,2,4,)-TMB systems of various mixing ratios, the mole fraction of 1,3,5-TMB in the total TMBs precipitated was considerably lower than that of 1,2,3- or 1,2,4-TMB: selective precipitation of 1,2,3- or 1,2,4-TMB occurred in the presence of 1,3,5-TMB. The concentration of α-CyD in the supernatant aqueous solution was determined as a function of the isomer mixing ratio. The selectivity was rather poor in the cases of TCB systems. Ternary mixtures of TMB isomers were also studied to a less extent. The solubility product constants at 25 °C were proposed for TMB and TCB precipitates with α-CyD.

Cyclodextrins (CyD's), cyclic oligosaccharides with central cavities, have unique properties. A variety of molecular species are held in an aqueous medium as guests inside the cavity. CyD's, themselves, are rather hydrophilic, but can be precipitated from aqueous solution in the presence of particular guests by forming inclusion complexes. This depends on the CyD-guest combination as well as on the CyD concentration in aqueous solution as to whether or not precipitation really occurs. To date, the guest/CyD molar ratio in the precipitates and the solubilities of CyD's in water in the presence of various guest substances (CyD concentrations in supernatant aqueous solutions after separation of CyD precipitates) have been studied.[1—5] These studies, however, were carried out with a single guest substance, and research concerning mixed-guest systems have received much less attention.

We recently proposed a vapor-circulation method to prepare CyD precipitates.[5—8] This method involves the vaporization of a guest substance and a continuous supply of guest molecules to an aqueous CyD solution by circulating the guest vapor in a closed system. Relatively pure CyD precipitates can be prepared by this method, because the formed precipitates are not in direct contact with an excess guest phase. Although the vapor-circulation method is only applicable to volatile guests, it is nevertheless useful for studying CyD-guest systems in water, because the concerned guests in such systems are usually hydrophobic volatile substances.

CyD precipitates with various volatile guests were prepared by means of the vapor-circulation method, and their guest/CyD molar ratios were determined in our previous studies.[5,8] It was observed that each of three trimethylbenzene (TMB) isomers was precipitated with β- and γ-CyD's, while 1,3,5-TMB was not precipitated with α-CyD, even at a CyD concentration near to saturation in water.[8] This observation suggests such a possibility that 1,2,3- or 1,2,4-TMB may be selectively precipitated with α-CyD from water in the presence of 1,3,5-TMB. We also studied whether or not such selective precipitation occurs among trichlorobenzene (TCB) isomers. This paper is additionally concerned with an evaluation of the solubility product constants of CyD precipitates (such constants, to our knowledge, have not been reported).

Experimental

Reagents. All of the reagents used were of analytical reagent grade. Deionized distilled water was used throughout the experiments. α-CyD of guaranteed grade (Nacalai Tesque Co.) was dried over phosphorus pentoxide under a vacuum.

Apparatus and Procedures. The procedure used to prepare CyD precipitates was described in a previous paper.[5] An α-CyD solution of less than 500 cm^3 was placed in a cylindrical separatory funnel (6.5 cm i.d., 600 cm^3 capacity) and ca. 20 cm^3 of the mixed guest solution was placed in a test tube (2.8 cm i.d.×25 cm). In the case of the (1,3,5–1,2,3)-TCB binary system, where two isomers were present in the solid state at the temperature studied, each equal quantity was simply transferred to a test tube and ca. 20 cm^3 of water was added. With the aid of a Viton diaphragm air pump (Iwaki Co., AP-032Z), air was introduced into the guest solution in the test tube via a glass capillary, and the resulting guest vapor was dispersed in the CyD solution via a glass capillary, and circulated in a closed system. The temperature of the CyD solution was held at 25.0±0.1 °C and that of the mixed-guest phase at 23.5 °C, or at 25.0 °C in the case of the (1,3,5–1,2,3)-TCB mixture by circulating water from two separately thermostated water baths through each jacket surrounding the funnel and the test tube. It was necessary to hold the temperature of the liquid guest mixture lower than that of the CyD solution to prevent guest-contamination of the formed CyD precipitate;[5] this was unnecessary for a solid guest mixture (contamination due to condensation of guest molecules in the CyD precipitate was not observed).

The CyD solution became turbid in most cases within one hour after vapor-circulation of the mixed-guest hydrocarbon; it took a longer time at lower CyD concentrations and at higher molar ratios of 1,3,5-TMB in the binary TMB mixtures. After the prescribed vapor-circulation times, a portion of the turbid CyD solution (less than 10 cm^3) was withdrawn to a centrifuge tube of 10 cm^3 capacity and then centrifuged at 4000 rpm for 10 min in order to separate the formed CyD precipitate. The guest hydrocarbons in the precipitate were extracted with cyclohexane and analyzed with a Shimadzu GC-14B gas chromatograph, operated at 140 °C using a fused silica wide-bore capillary column of 0.53 mm×25 m, coated with poly(dimethylsiloxane). *m*-Xylene and 1,2,4-TMB were used as internal standards for analyses of TMBs and TCBs, respectively. The amount of CyD in the precipitates and the CyD concentration in the supernatant aqueous solutions were determined by a Shodex Model SE-11 differential refractometer.

Solubility of Guest Substances in Water. In the absence of CyD, aqueous solutions saturated with the vapor of the mixed-guest of various mixing ratios were prepared by the vapor-circulation method, and the solubilities of the guests in water were determined. These solubility data, which correspond to the concentrations of free guests (not associated with CyD), were necessary to estimate the concentrations of the guest species associated with CyD in equilibrium and to determine the solubility product of the formed precipitates.

Results and Discussion

Mixtures of Trimethylbenzene Isomers. Precipitations of mixed guests with α-CyD occur in aqueous solutions, where guest substances are dissolved through circulating the vapor of the mixed-guest phase. It is, therefore, important to know how each guest substance attains a constant concentration in water as a function of the vapor-circulation time, and how its concentration changes with the mixing ratio of the guest phase. It has been confirmed for all of the TMB and TCB mixed-systems studied in this work that each constituent component attains a constant concentration in water within 30 min. This means that the isomer composition in the CyD precipitated after one hour of vapor circulation is independent of the circulation time.

The concentrations of the TMB isomers in CyD-free water are shown in Figs. 1A and 1B as a function of the mole fraction of the mixed-guest phase ($X_{1,2,3\text{-TMB}}$ or $X_{1,2,4\text{-TMB}}$). It is clear that 1,3,5-TMB forms an ideal solution with 1,2,3- or 1,2,4-TMB. We hereafter use [ϕ], [ϕ'], and [ϕ''] as the free guest molar concentrations (1 M≡1 mol dm^{-3}), where ϕ, ϕ', and ϕ'' refer to 1,3,5-, 1,2,3-, and 1,2,4-TMB, respectively.

From the supernatant CyD concentrations ($[CyD]_s$), shown in Fig. 2 as a function of *X* or free guest concentration, the free CyD concentrations ([CyD]) are derived as follows:

$$[CyD] = [CyD]_s - [CyD\cdot\phi] - [CyD\cdot\phi'] - 2[CyD_2\cdot\phi'], \quad (1)$$

for the (1,3,5–1,2,3)-TMB system and

$$[CyD] = [CyD]_s - [CyD\cdot\phi] - [CyD\cdot\phi''], \quad (2)$$

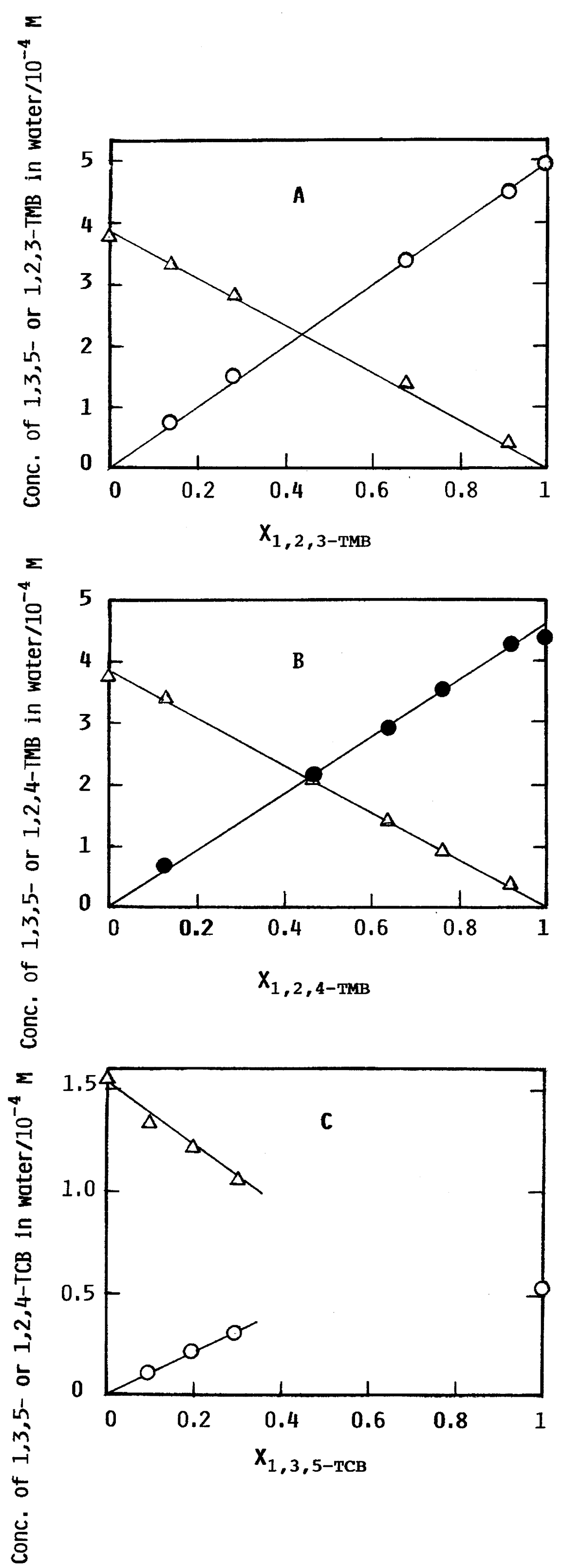

Fig. 1. Concentrations in water in the absence of CyD at 25 °C of the constituent components of binary mixed-guests as a function of the component mole fraction. A: (1,3,5 (△)–1,2,3 (○))-TMB system; B: (1,3,5 (△)–1,2,4 (●))-TMB system; C: (1,3,5 (○)–1,2,4 (△))-TCB system. Temperature of the mixed-guest phase: 23.5 °C. *X* is the mole fraction of the subscript component in the mixed-guest phase.

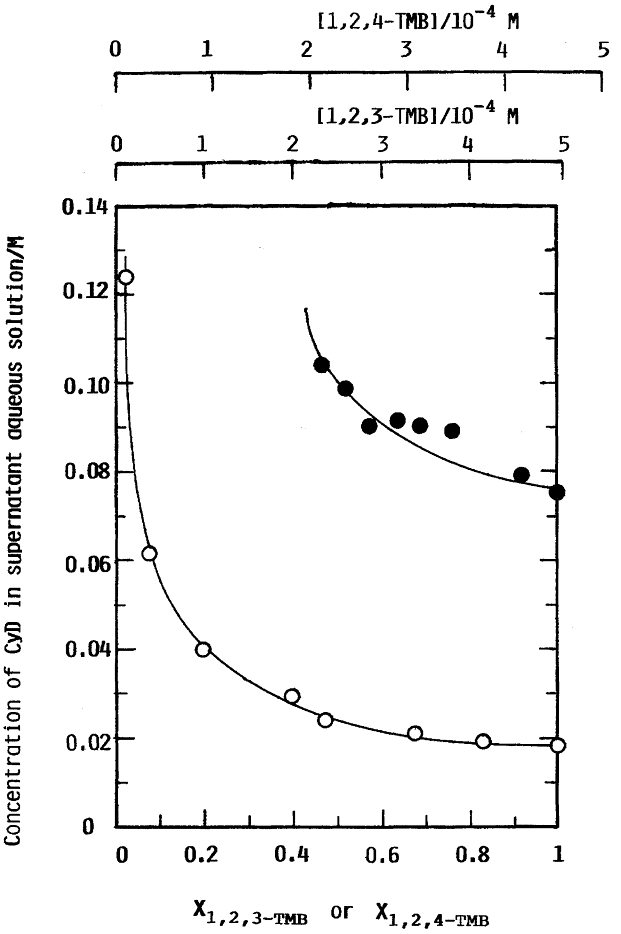

Fig. 2. Concentrations of α-CyD in supernatant aqueous solutions. ○: (1,3,5–1,2,3)-TMB system; ●: (1,3,5–1,2,4)-TMB system. [TMB] on the above abscissa refers to the free TMB concentration determined from Figs. 1A and 1B.

for the (1,3,5–1,2,4)-TMB system. The equilibria that must be taken into account are as follows:

$$[\mathrm{CyD}] + \phi \rightleftharpoons \mathrm{CyD}\cdot\phi, \qquad K_1 = 61\ \mathrm{M}^{-1}, \tag{3}$$

$$[\mathrm{CyD}] + \phi' \rightleftharpoons \mathrm{CyD}\cdot\phi', \qquad K'_1 = 13\ \mathrm{M}^{-1}, \tag{4}$$

$$[\mathrm{CyD}]\cdot\phi' + \mathrm{CyD} \rightleftharpoons \mathrm{CyD}_2\cdot\phi', \quad K'_2 = 470\ \mathrm{M}^{-1}, \tag{5}$$

and

$$[\mathrm{CyD}] + \phi'' \rightleftharpoons \mathrm{CyD}\cdot\phi'', \qquad K''_1 = 46\ \mathrm{M}^{-1}. \tag{6}$$

The association constant data are taken from our previous paper;[9] those of 2 : 1 (CyD : guest) complexes for 1,3,4- and 1,2,4-TMBs are not reported in the literature.

The concentrations of all the species present in the supernatant aqueous solutions in equilibrim with the precipitates are given in Tables 1 and 2. The mole fractions of 1,2,3-TMB ($X'_{1,2,3\text{-TMB}}$) and 1,2,4-TMB ($X'_{1,2,4\text{-TMB}}$) in the total TMBs present in the aqueous phase are given in Table 1. These values were estimated by $X'_{1,2,3\text{-TMB}}=A/(A+C)$ and $X'_{1,2,4\text{-TMB}}=B/(B+C)$:

$$A = [\phi'] + [\mathrm{CyD}\cdot\phi'] + [\mathrm{CyD}_2\cdot\phi'], \tag{7}$$

$$B = [\phi''] + [\mathrm{CyD}\cdot\phi''], \tag{8}$$

and

$$C = [\phi] + [\mathrm{CyD}\cdot\phi]. \tag{9}$$

Due to a large contribution of $[\mathrm{CyD}_2\cdot\phi']$, the $X'_{1,2,3\text{-TMB}}$ value is considerably larger than the corresponding $X_{1,2,3\text{-TMB}}$, and the [CyD] values differ from the $[\mathrm{CyD}]_\mathrm{s}$ by 4 to 10% in the (1,3,5–1,2,3)-TMB system, while, in the (1,3,5–1,2,4)-TMB system the difference is only 2%. For a reference, the isomer mole fractions in the total TMBs in the aqueous phase in the absence of CyD are shown in the parentheses in Table 1.

The isomer compositions in CyD precipitates are summarized in Table 1. The compositions were independent of both the vapor-circulation time and the concentration of CyD in the initial solution ($[\mathrm{CyD}]_0$). As the $X'_{1,2,3\text{-TMB}}$ or $X'_{1,2,4\text{-TMB}}$ value decreases, the mole fraction of the 1,2,3- or 1,2,4-TMB in TMB contents of the CyD precipitate decreases. This is probably due to a coprecipitation of 1,3,5-TMB. A sufficiently long vapor-circulation time was of no use to reduce the fraction of 1,3,5-TMB in the precipitate. Aging seems not to work in its original sense in the present cases, since guest molecules are continuously supplied by vapor-circulation during "aging".

Solubility Product and Precipitation. Let us consider the following precipitation reaction:

$$\mathrm{CyD} + n\Phi \rightleftharpoons \mathrm{CyD}\cdot\Phi_n(\mathrm{s}), \tag{10}$$

where Φ refers to a guest molecule. Then, the solubility product (K_sp) is expressed as follows:

$$K_\mathrm{sp} = [\mathrm{CyD}][\Phi]^n. \tag{11}$$

Using the data given in Tables 1 and 2, $-\log[\mathrm{CyD}]$ are plotted against $-\log[\phi']$ or $-\log[\phi'']$ in Fig. 3. From the least-squares method, we obtain 7.6×10^{-4} (K_sp) and 0.40(n) for 1,2,3-TMB and 4.0×10^{-3} (K_sp) and 0.38(n) for 1,2,4-TMB. In the case of 1,2,3-TMB, the least-squares method was applied only to four data in the lower [CyD] range for two reasons: these four data are on a good straight line (the solid line in Fig. 3) and the obtained n value is in reasonable agreement with the experimentally determined guest/CyD molar ratio in the precipitate (Table 1). If all of the data (eight) are used (the dotted line in Fig. 3), we obtain 2.6×10^{-4} (K_sp) and 0.54(n) for 1,2,3-TMB. In the case of 1,2,4-TMB, [CyD] being nearly equal to $[\mathrm{CyD}]_\mathrm{s}$, this can be satisfactorily used for estimating K_sp.

We now consider a situation in which a sufficient quantity of the α-CyD–1,2,3-TMB precipitate is transferred to fresh water of a definite volume. With the K_sp ($=7.6\times10^{-4}$) for $\mathrm{CyD}\cdot\phi'_{0.40}$, the [CyD] and $[\phi']$ are estimated from the solubility of the precipitate to be $(7.7 \text{ and } 3.1)\times10^{-3}$ M, respectively, provided that the precipitate completely dissociates into CyD and ϕ'. The thus-estimated $[\phi']$ is six-times larger than the solubility of ϕ' in water, and, hence, the excess amount of ϕ' should be excluded from the aqueous

Table 1. 1,3,5-Trimethylbenzene–(1,2,3 or 1,2,4)-Trimethylbenzene Binary Mixed System

Mole fraction of 1,2,3- or 1,2,4-TMB in total TMBs			Concentration of α-CyD/mol dm^{-3}			Molar ratio of
Mixed-guest phase (X)	Aqueous solution$^{a)}$ (X')	Ppt. with CyD	Initial solution ([CyD]$_0$)	Supernatant solution ([CyD]$_s$)	[CyD]$^{b)}$	(TMB/CyD) in ppt.
1,2,3-TMB:						
0	0 (0)	—$^{c)}$	0.140		0.137	
0.026	0.27(0.034)	0.90	0.130	0.124	0.119	0.31
0.079	0.36(0.10)	0.96	0.130	0.0615	0.0586	0.37
0.198	0.50(0.24)	0.98	0.100	0.0400	0.0376	0.42
0.398	0.65(0.46)	0.98	0.122	0.0292	0.0270	0.43
0.471	0.68(0.54)	0.99_2	0.0519	0.0241	0.0223	0.39
0.673	0.81(0.73)	0.99_5	0.0445	0.0210	0.0193	0.40
0.831	0.91(0.86)	0.99_8	0.0478	0.0193	0.0176	0.42
1	1 (1)	1	0.0300	0.0183	0.0165	0.39
1,2,4-TMB:						
0	0 (0)	—$^{c)}$	0.140		0.137	
0.129	0.12(0.15)	—$^{c)}$	0.121		0.118	
0.259	0.24(0.29)	—$^{c)}$	0.123		0.120	
0.380	0.36(0.42)	—$^{c)}$	0.122		0.119	
0.468	0.45(0.51)	0.97	0.127	0.104	0.102	0.29
0.514	0.50(0.56)	0.97	0.125	0.0988	0.0967	0.28
0.571	0.56(0.61)	0.97	0.123	0.0900	0.0881	0.24
0.639	0.62(0.68)	0.97	0.112	0.0916	0.0897	0.34
0.685	0.67(0.72)	0.98	0.122	0.0907	0.0888	0.35
0.760	0.75(0.79)	0.99_0	0.120	0.0894	0.0875	0.31
0.919	0.91(0.93)	0.99_7	0.110	0.0790	0.0774	0.34
1	1 (1)	1	0.120	0.0751	0.0736	0.32

a) $X'_{1,2,3\text{-TMB}}=A/(A+C)$ and $X'_{1,2,4\text{-TMB}}=B/(B+C)$, where A, B, and C are noted in the text (Eqs. 7, 8, and 9). Those shown in the parenthese are isomer mole fractions in the absence of α-CyD, which can be estimated from Table 2, $[\phi']/([\phi']+[\phi])$ for 1,2,3-TMB and $[\phi'']/([\phi'']+[\phi])$ for 1,2,4-TMB. b) [CyD] refers to the CyD concentration in the free form (see Eqs. 1 and 2 in the text). c) Precipitation (ppt.) does not occur.

phase; to compensate for the lack of ϕ', the precipitate further dissolves to give a higher [CyD] until it amounts to 0.016 M. The most striking feature of the precipitation of organic nonelectrolytes with CyD is the extremely small solubility of nonelectrolytes in water.

The experimentally determined guest/CyD molar ratios in the precipitates (Table 1) tend to be more or less underestimated, owing to contamination by the CyD present in supernatant solutions. It is, indeed, impossible to completely remove water (supernatant solution) from the precipitate by centrifugation. The concentrations of guest in supernatant solutions are low enough to be neglected, while those of CyD are relatively high. The water contents in the precipitates were in the 0.1 to 0.9 cm^3 range, depending on the amount of the precipitate formed, that is, $([\text{CyD}]_0-[\text{CyD}]_s)\times 10$ mmol, if a 10 cm^3 portion of the turbid CyD solution was taken to a centrifuge tube. The contributions of the contaminated CyD, $(0.1 \text{ to } 0.9)\times[\text{CyD}]_s$ mmol, to the guest/CyD molar ratios were estimated to be 7 to 11% in the case of 1,2,4-TMB and 20% at the highest [CyD]$_s$ in the case of 1,2,3-TMB. When we consider these experimental errors, the n value obtained by the least-squares method based on Eq. 11 seems to be reasonable.

It is difficult, as described in the previous paper,[8] to explain why 1,3,5-TMB does not precipitate in an α-CyD solution, while the other two isomers do precipitate. The total amount of 1,3,5-TMB dissolved in water, the sum of $[\phi]$ and $[\text{CyD}\cdot\phi]$ in Table 2, is comparable to that of 1,2,4-TMB. The 1 : 1 associated complex formation constant (K_1) is rather larger than K'_1 or K''_1. Therefore, neither the population of the guest species nor the affinity of guest molecules for α-CyD in the aqueous phase seems to be responsible for the formation of precipitation. To date, the mechanism of the CyD–guest precipitation formation in water has not been discussed in the literature. Here, we try to explain the mechanism based on aggregation.

A guest molecule (Φ) associates at first with CyD to form complex(es), such as $\text{CyD}\cdot\Phi$ (and $\text{CyD}_2\cdot\Phi$), then, the associated species aggregate with each other or, more likely, with free CyD molecules, which are present far more abundantly than the guest species, and finally, the larger aggregates formed precipitate. This aggregation tendency, which may be related to the structure of the guest molecule and/or the CyD-associated species, may differ from guest to guest.

Table 2. Guest Species Present in Supernatant Aqueous Solution Under Conditions Shown in Table 1

Mole fraction of guest (X)	Concentration of guest species in aqueous solution in equilibrium with CyD precipitate[a)]/10^{-4} mol dm^{-3}				
	$[\phi']$ or $[\phi'']$	$[\phi]$	$[\mathrm{CyD}\cdot\phi']$ or $[\mathrm{CyD}\cdot\phi'']$	$[\mathrm{CyD}_2\cdot\phi']$	$[\mathrm{CyD}\cdot\phi]$
1,2,3-TMB:					
0	0	3.82	0	0	31.9
0.026	0.13	3.72	0.20	11.2	27.0
0.079	0.39	3.52	0.30	8.24	12.6
0.198	0.98	3.06	0.48	8.48	7.01
0.398	1.98	2.30	0.69	8.80	3.79
0.471	2.34	2.02	0.68	7.13	2.75
0.673	3.34	1.25	0.84	7.57	1.47
0.831	4.13	0.65	0.94	7.80	0.70
1	4.97	0	1.07	8.30	0
1,2,4-TMB:					
0	0	3.82	0		31.9
0.129	0.58	3.33	3.16		24.0
0.259	1.17	2.83	6.47		20.8
0.380	1.72	2.37	9.44		17.2
0.468	2.12	2.04	10.0		12.6
0.514	2.33	1.86	10.4		11.0
0.571	2.59	1.64	10.5		8.81
0.639	2.89	1.38	11.9		7.55
0.685	3.10	1.21	12.7		6.55
0.760	3.44	0.92	13.8		4.91
0.919	4.16	0.31	14.8		1.46
1	4.53	0	15.3		0

a) The signs ϕ, ϕ', and ϕ'' refer to 1,3,5-, 1,2,3-, and 1,2,4-TMB, respectively. These free guest concentrations, $[\phi]$, $[\phi']$, and $[\phi'']$, were estimated from Figs. 1A and 1B.

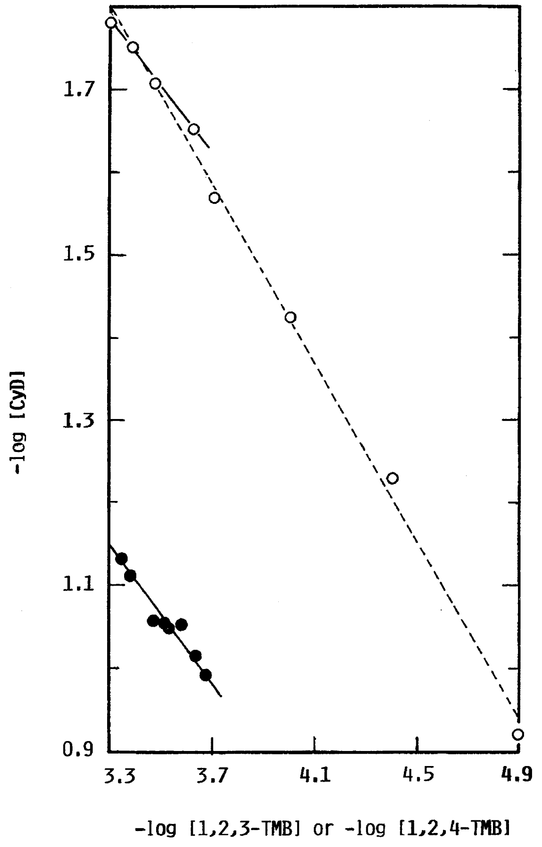

Fig. 3. Plots of $-\log[\mathrm{CyD}]$ vs. $-\log[\mathrm{TMB}]$. [CyD] and [TMB] refer to the free CyD and TMB concentrations in supernatant solutions, respectively. ○ and ●: See Fig. 2.

The aggregation tendency of 1,3,5-TMB may be least among the TMB isomers.

Trimethylbenzene Ternary Mixed-System. The results are listed in Table 3. The main composition of TMBs in the precipitates was 1,2,3-TMB; next, it was 1,2,4-TMB. We employed two different $[\mathrm{CyD}]_0$, 0.0490 and 0.120 M.

Runs were made only at an equal isomer composition in the mixed-guest phase. Under such a condition, the free guest concentrations were determined from Figs. 1A and 1B and based on the assumption that the three isomers form an ideal solution: 1.27 ($[\phi]$), 1.66 ($[\phi']$), and 1.51×10^{-4} M ($[\phi'']$). The mole fraction of each component in total TMBs dissolved in the aqueous phase was estimated based on Equilibria 3 to 6 being 0.21 (1,3,5-), 0.58 (1,2,3-), and 0.21 (1,2,4-TMB). The [CyD] was estimated to be nearly equal to the $[\mathrm{CyD}]_\mathrm{s}$ (=0.026 M) as follows:

$$[\mathrm{CyD}] = [\mathrm{CyD}]_\mathrm{s} - [\mathrm{CyD}\cdot\phi] - [\mathrm{CyD}\cdot\phi'] - 2[\mathrm{CyD}_2\cdot\phi'] - [\mathrm{CyD}\cdot\phi''] = 0.0255. \tag{12}$$

Another way to estimate the [CyD] value is to use the K_sp

Table 3. Trimethylbenzene Ternary Mixed System with Equal Mole Fraction[a)]

Concentration of α-CyD/mol dm^{-3}		Mole fraction in sum of three TMBs precipitated			Molar ratio of
Initial solution ($[\mathrm{CyD}]_0$)	Supernatant solution ($[\mathrm{CyD}]_\mathrm{s}$)	1,3,5-TMB	1,2,3-TMB	1,2,4-TMB	(TMB/CyD) in ppt.
0.0490	0.0264	0.008	0.88_9	0.10_3	0.39
0.120	0.0259	0.007	0.83_3	0.16_0	0.40

a) Three isomers in an equal weight were mixed. Isomer mole fractions in the total TMBs dissolved in aqueous solutions (X') estimated at $[\mathrm{CyD}]_\mathrm{s}$ are 0.21 (1,3,5-), 0.58 (1,2,3-), and 0.21 (1,2,4-TMB). Concentrations of isomer in aqueous solutions in the absence of α-CyD, $[\phi]$, $[\phi']$, and $[\phi'']$, are $(1.27, 1.66, \text{and } 1.51)\times10^{-4}$ M, respectively.

Table 4. Precipitation of Single and Mixed Trichlorobenzene

Single or	Mole fraction of 1,2,3- or 1,2,4-TCB in total TCBs			Concentration of α-CyD/mol dm^{-3}		Molar ratio of
mixed-guest system	Mixed-guest phase	Aqueous solution[a]	Ppt. with CyD	Initial solution ($[\mathrm{CyD}]_0$)	Supernatant solution ($[\mathrm{CyD}]_s$)	(TCB/ CyD) in ppt.
Single–guest system:						
1,3,5-TCB				0.100	0.080	0.30
1,2,3-TCB				0.0500	0.019	0.44
1,2,4-TCB				0.0705	0.028	0.38
Mixed–guest system:						
(1,3,5–1,2,3)-TCB						
	0.500	(0.65)	0.88	0.0500	0.020	0.40
	0.500	(0.65)	0.70	0.100	0.020	0.39
(1,3,5–1,2,4)-TCB						
	0.602	(0.68)	0.84	0.0500	0.030	0.37
	0.602	(0.68)	0.76	0.100	0.035	0.23
	0.738	(0.80)	0.89	0.0700	0.030	0.35
	0.738	(0.80)	0.86	0.100	0.030	0.27
	0.808	(0.86)	0.92	0.0500	0.029	0.38
	0.808	(0.86)	0.90	0.100	0.029	0.36
	0.926	(0.95)	0.97	0.0700	0.030	0.23
	0.926	(0.95)	0.95	0.100	0.032	0.24

a) Isomer mole fractions in the presence of α-CyD cannot be determined, because of the lack of the TCB–CyD association constant data. Those shown in the parenthese are isomer mole fractions in the absence of α-CyD.

value of $\mathrm{CyD}\cdot\phi'_{0.40}$ or $\mathrm{CyD}\cdot\phi''_{0.38}$ (Eq. 11). In this case, we can judge which precipitate predominates. The [CyD] estimated from $\mathrm{CyD}\cdot\phi'_{0.40}$ is 0.025 M and that from $\mathrm{CyD}\cdot\phi''_{0.38}$ is 0.11 M. Since the former is equal to that estimated by Eq. 12, precipitation is governed by 1,2,3-TMB in the ternary mixed-system of TMB isomers. In view of the K_{sp} of 1,2,4-TMB, this guest was expected not to be precipitated at $[\mathrm{CyD}]_s$ as low as 0.026 M.

Contrary to our expectation, however, the fraction of 1,2,4-TMB in the total TMBs precipitated was as high as 16 or 10%, depending on $[\mathrm{CyD}]_0$ (Table 3). These fractions are too high to be explained in terms of coprecipitation. No simple explanation for the precipitation of 1,2,4-TMB observed in the ternary system can be offered at the present time. A possible explanation is that the guest/CyD molar ratio and the solubility product of the 1,2,4-TMB precipitates formed in the presence and absence of 1,2,3-TMB differ from each other. That is, these two parameters are no longer applicable to the CyD–guest species in a precipitation process, where precipitation is governed by a less soluble species.

Mixtures of Trichlorobenzene Isomers. Of three TCB isomers, 1,3,5- and 1,2,3-TCBs exist as a solid at room temperature, and hence, isomer binary mixtures to be prepared are in limited composition ranges. In the (1,3,5–1,2,3)-TCB binary system, an equal amount of the isomer was mixed and used as a mixed-guest phase. In this case, the solubility of each component in water was found to be independent of the mixing ratio and equal to its own solubility: 1,3,5 (5.33×10^{-5}) and 1,2,3 (1.01×10^{-4} M) at 25 °C. In the (1,3,5–1,2,4)-TCB system, the solubility of 1,3,5-TCB in 1,2,4-TCB can be estimated as follows:

$$\ln X = \Delta H_{\mathrm{f}}\, \mathrm{R}^{-1}(1/T_{\mathrm{f}} - 1/T), \tag{13}$$

where R is the gas constant (8.31441 J mol^{-1} K^{-1}). Using the data for 1,3,5-TCB,[10] 18.198 kJ mol^{-1} as ΔH_{f} (molar heat of fusion) and 336.65 K as T_{f} (melting point), we get 0.42 as X (mole fraction solubility) at 23.5 °C. This solubility is an approximate one, because the molar heat capacity of 1,3,5-TCB was neglected in Eq. 13 and the heat of fusion was assumed to be constant. We studied the (1,3,5–1,2,4)-TCB system at mole fractions of 1,2,4-TCB larger than 0.6.

The isomer compositions in CyD precipitates are summarized in Table 4. The selectivity in precipitation was quite poor. In the single guest system, the $[\mathrm{CyD}]_s$ decreases in the order 1,3,5-, 1,2,4-, and 1,2,3-TCB. That is, 1,3,5-TCB is most difficult to precipitate and does not precipitate at a $[\mathrm{CyD}]_0$ below 0.080 M, if this guest alone is present in the CyD solution. In binary systems, however, 1,3,5-TCB precipitates at $[\mathrm{CyD}]_s$ well below 0.080 M together with 1,2,3- or 1,2,4-TCB to a considerable extent. This situation is similar to that of the TMB ternary mixed-system.

Although we have shown above the aqueous solubility data for each TCB isomer (1.52×10^{-4} M for 1,2,4-TCB at 25 °C), we cannot give any information about the TCB species associated with CyD and their concentrations, because no data concerning any CyD–TCB association constants are available in the literature. Here, we roughly estimate the solubility product constant at 25 °C for the precipitates, $CyD \cdot TCB_n$, by assuming $[CyD]_s$ being nearly equal to [CyD]: 4.2×10^{-3} for 1,3,5-TCB (n=0.30), 3.3×10^{-4} for 1,2,3-TCB (n=0.44), and 9.9×10^{-4} for 1,2,4-TCB (n=0.38).

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