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Volumetric study on the inclusion complex formation of α - and β -cyclodextrin with 1-alkanols at different temperatures

Received: 5 April 2004
Accepted: 4 September 2004
Published online: 2 December 2004
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Abstract The partial molar volumes (V_a) of 1-alkanols (carbon number, $m = 5, 6, 7$) in α - and β -cyclodextrin (CD) solutions at 5.00 mmol kg⁻¹ have been determined as a function of alkanol concentration (C_a) between 293.2 and 308.2 K by using a dilatometer. It has been observed that with an increase in C_a , V_a increased in α -CD solution but decreased in β -CD solution, asymptotically to a value of V_a in CD-free water. The dependence of V_a on C_a provided the binding constant (K) of 1:1 complex, the volume change in complex formation, and the partial molar volume of complex itself. The complex formation

mechanism has been discussed on the basis of these values and their carbon number dependences in the respect of geometric behavior, hydrophobic interaction, and van der Waals interaction. It is concluded that the CD cavity in water is not rigid but flexible for fitting in nicely with guest molecule.

Keywords Cyclodextrin · Alcohol · Inclusion complex · Partial molar volume · Binding constant · Temperature dependence · Volume

Introduction

Cyclodextrins (cycloamyloses), (CD), consist of several α -D-glucopyranose units in order to form a cylindrical cavity, which is hydrophobic from inside and hydrophilic from outside. The structural characteristic leads to the formation of an inclusion complex by accommodating a variety of hydrophobic guests in the cavity [1]. Accordingly, a variety of CD complexes have been studied in the area of both chemistry [2] and industry [3]. Based on the hydrophobicity, the hydrophobic interaction as well as the cavity size are the governing factors for the complex formation between the cavity and the guest molecule in comparison with the conformational change of the CD cavity, hydration, and electrostatic effect.

The inclusion mechanism of a guest in the CD cavity has geometric aspect. Therefore, volumetric study on the

complex formation is instructive. The volumetric data provides good insight not only into the structure but also to the nature of the interactions and solvation behavior of the host-guest systems. In addition, volumetric study has an advantage that without any chromophore in the guest molecules necessary for spectroscopic detection, the binding constant of the CD complex can be determined. However, there have been only a few volumetric studies of CD complexes [4–12].

The extensive studies of hydrophobic interaction have been carried out in the area of micelle formation of surfactant and solubilization systems. In order to estimate the hydrophobicity of the alkyl-chain, a homologous series of substances are useful, since the hydrophobicity continuously changes with the carbon number. According to the carbon number dependence of the partition coefficient of homologous 1-alkanols [13, 14] and alkanediols [14] between water and micellar

phases, the three CH₂ groups nearest to the OH group are rather hydrophilic, and the other CH₂ groups far apart are hydrophobic. This indicates that the mechanism of CD complex formation with the longer chain alkanols than propanol are different from the shorter ones, with respect to the hydrophobic interaction of complex formation.

In the present study, the partial molar volume (PMV) of 1-alkanols (carbon number $m=5, 6, 7$) in α - and β -CD solution at a given CD concentration (5 mmol kg⁻¹) between 293.2 and 308.2 K was determined as a function of alkanol concentration. A dilatometric method was applied, which allows us to determine PMV even at higher dilution more precisely compared to the widely used densimetry.

Experimental

Materials

α - and β -Cyclodextrins (CD) supplied by Ensuiiko Sugar Refining Co. Ltd. were dried in a vacuum electric oven about 382.2 K for 1 day in order to completely dehydrate the CD [15]. 1-Alkanols (carbon number, $m=5, 6, 7$) purchased from Tokyo Kasei (GR grade) were used without further purification. All solutions were prepared using degassed, deionized, and distilled water.

Procedure

Partial molar volume of 1-alkanols (V_a) in CD solution (concentration: $C_d=5.00$ mmol kg⁻¹) was measured as a function of alkanol concentration (C_a) by the same dilatometric method described in detail in our previous paper [16]. The used dilatometer consisted of a glass bulb (ca. 500 cm³) and a capillary (ca. $\phi 1.8$ mm, 20 cm long). When measuring PMV, small amounts of alkanol (ca. 40 mg) were successively injected, by weight, into the dilatometer bulb filled with the CD solution, and then the volume increment in the capillary was read by a cathetometer to an accuracy of 1/100 mm. The value of V_a was taken to be the volume increment divided by the mole numbers of injected alkanol. Each measurement was made at least more than 1 h after injection. The maximum concentration of alkanols in the measurements is shown in Table 1. In some systems, the solution was very slightly turbid above a C_a given in Table 1, even though stirred for more than 1 h on each addition, but the characteristic volumetric behavior due to turbidity was not observed. The temperature of the water bath was controlled within $\pm 1/1,000$ K by detecting a thermistor-bridge circuit, at each measuring temperature (293.2, 298.2, 303.2, and 308.2 K).

Results and discussion

Dependence of V_a on C_a

The PMV of alkanols in water had little concentration dependence (Fig. 1). Then, the mean value was taken to be the PMV of alkanol in water, V_{aw} , and is listed in Table 1. Each V_{aw} value at 298.2 K is in good agreement with that of the previous study [13]. When CD is present, the PMV of alkanol, V_a , exhibits a characteristic concentration dependence. The V_a as a function of C_a of heptanol at the constant C_d is illustrated in Fig. 1. As for α -CD, V_a increases asymptotically toward the value of V_{aw} in the sigmoid form. On the contrary, for β -CD, V_a decreases asymptotically in a symmetric form to the value in α -CD. It is surprising that only one glucopyranose unit difference in CDs leads to such an opposite C_a dependence. Each sigmoid form reflects an equilibrium reaction of the complex formation. A few volumetric studies on the ternary systems of β -CD-surfactant aqueous solution have been carried out by densimetry [6, 8, 9, 12].

Wilson and Verrall reported the apparent molar volume (AMV) of hydrocarbon and fluorocarbon surfactants in the solution of β -CD [9] as well as modified β -CD [12] as a function of the surfactant concentration below the critical micelle concentration, where the pattern of each curve is sigmoid with decreasing tendency. In addition, in the presence of β -CD, the AMV of anionic and cationic surfactants in pre-micellar region is higher than that in the CD-free solution [6, 9]. Even for some simple inorganic salts, the AMV of extrapolated value to limiting dilution for the guests in β -CD solution is higher than or close to that in water [4]. On the contrary, in the systems of α -CD-homologous amphiphiles, no volumetric study was performed, except for the same simple inorganic salts [4]. These reported results are compatible with the present ones of the concentration dependence for each CD. All these results including the present ones, lead to the conclusion that for various guests such as nonionic, ionic amphiphiles, and even simple anions, the volume change on complex formation is positive in β -CD and negative in α -CD.

Determination of binding constant (K)

The binding constant (K) was calculated on the basis of volumetric data by the following procedure. It is apparent that the C_a around each inflection point of the sigmoid curve in Fig. 1 is numerically close to C_d in each system studied, indicating the formation of the complex of 1:1 composition. Then, by assuming the 1:1 complex formation, K can be determined. When free monomer alkanol (A_f) and free CD (D_f)

Table 1 Binding constant and volumetric data for complex formation of α - and β -CD with 1-alkanols

T/K	m	K (l mol ⁻¹)	ΔV (cm ³ mol ⁻¹) ^g	V_{af} (cm ³ mol ⁻¹) ^h	V_{aw} (cm ³ mol ⁻¹) ⁱ	$C_a(\text{max})$ (mmol l ⁻¹) ^j	Turbid ^k
[α -CD]							
288.2	5	374 ^a					
288.2	6	913 ^a					
288.2	7	1,490 ^a					
293.2	5	1,100	-2.31	100.97	101.49	31.6	
293.2	6	2,260	-4.67	118.08	117.51	16.5	7.6
293.2	7	3,800	-5.40	131.78	132.31	12.0	
298.2	5	500	-4.26	101.85	102.44	26.5	16.2
		245 ^a					
		275 ^c					
		210 ^d					
298.2	6	1,100	-6.11	117.77	118.25	30.2	15.90
		703 ^a					
		379 ^c					
		940 ^d					
298.2	7	2,450	-7.66	133.82	134.23	28.2	19.1
		1,160 ^a					
		2,700 ^d					
303.2	5	252	-5.14	102.80	102.83	37.2	
303.2	6	480	-10.15	118.49	118.45	19.7	
303.2	7	1,100	-8.15	135.01	134.76	14.8	
308.2	5	80	-15.45	103.84	104.30	22.1	
		194 ^a					
308.2	6	220	-14.65	119.95	118.67	18.7	
		402 ^a					
308.2	7	520	-2.85	133.53	135.03	17.0	13.7
		792 ^a					
[β -CD]							
293.2	5	200	7.94	102.12	101.49	20.3	
293.2	6	320	16.44	117.70	117.51	13.7	6.3
293.2	7	760	20.06	132.50	132.31	15.5	6.1
298.2	5	300	5.18	102.73	102.44	23.7	
		63.1 ^b					
		76 ^c					
		62 ^f					
298.2	6	710	10.60	118.47	118.25	21.8	
		219 ^b					
		280 ^e					
298.2	7	1,550	12.06	133.81	134.23	13.9	7.2
		708 ^b					
		700 ^d					
		660 ^e					
		620 ^f					
303.2	5	98	13.72	103.06	102.83	77.3	
303.2	6	400	14.32	117.92	118.45	22.1	6.1
303.2	7	850	16.20	135.04	134.76	23.8	18.9
308.2	5	80	16.26	102.61	104.30	31.3	
308.2	6	200	19.29	118.23	118.67	17.4	
308.2	7	470	21.48	134.11	135.03	18.5	

Determined at

 $C_d = 5.00$ mmol kg⁻¹^aRef. [29]^bRef. [21]^cRef. [31]^dRef. [23]^eRef. [22]^fRef. [26]^g $\Delta V = V_x - V_{af} - V_{df}$ in Eq. 7^hCalculated value through

Eq. 7

ⁱExperimental value in water^jMaximum C_a in measuring V_a ^kSlightly turbid above this C_a

are in equilibrium with 1:1 complex (X), in the reaction



the concentrations of respective species are correlated as

$$C_a = C_{af} + C_x, \quad C_d = C_{df} + C_x \quad (2)$$

where the subscripts a and d denote alkanol and CD, and f and x represent the uncomplexed and complexed states, respectively. According to Eq. 1, K is defined as

$$K = \frac{C_x}{C_{af} \cdot C_{df}} \quad (3)$$

From Eqs.2 and 3, C_x can be calculated.

$$C_x = \frac{1}{2} \left[\left(C_a + C_d + \frac{1}{K} \right) - \left\{ \left(C_a + C_d + \frac{1}{K} \right)^2 - 4C_a C_d \right\}^{1/2} \right] \quad (4)$$

By differentiating C_x with C_a at a certain C_d , the differential denoted by J is derived.

$$\frac{dC_x}{dC_a} = J = \frac{C_d - C_x}{(C_a - C_x) + (C_d - C_x) + 1/K} \quad (5)$$

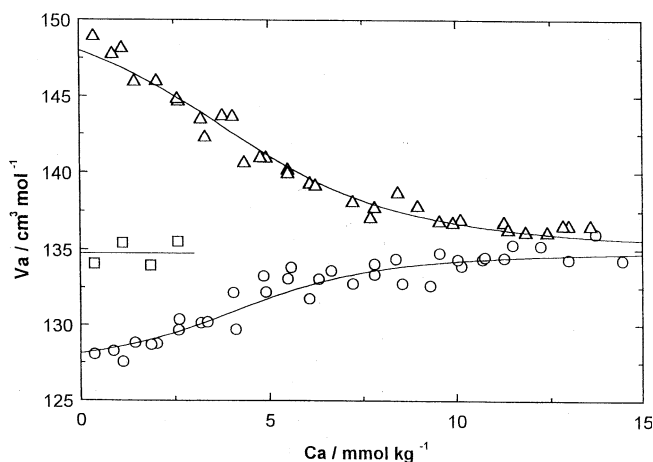


Fig. 1 The relation between PMV of heptanol and its concentration at 303.2 K. In water (*open square*), in α -CD solution (*open circle*), and in β -CD solution (*open triangle*). CD concentration is 5.00 mmol kg⁻¹. The line for CD solution indicates the V_a value calculated from K , ΔV , and V_{af} given in Table 1, and the line for water does averaged value

The quantity (J) implies the fraction of complex-form alkanol on each addition of alkanol.

On the other hand, the total volume (V) of a solution including alkanol and CD in 1 kg of water (n_w mol) is represented as the sum of volumetric contributions of respective species.

$$V = V_w n_w + V_{af} C_{af} + V_{df} C_{df} + V_x C_x \quad (6)$$

where V_i refers to PMV of each species, and V_{af} is, in the physical meaning, the same quantity as V_{aw} (V_a in water). In the present experimental condition, the concentration of each species is very low; $C_d = 5$ mmol kg⁻¹ and the maximum C_a is shown in Table 1. Then, the concentration dependence of each V_i can be assumed to be ignored, taking the following facts into account. The V_{aw} had little dependence on C_a (see Fig. 1) in the similar C_a region as in the CD solution. Further, for the concentration dependence of CD, the AMV of α -CD in water was almost constant up to 13 mmol kg⁻¹ at 298.2 K [9]. Accordingly, the PMV of alkanol corresponding to the experimentally determined quantity, $V_a = dV/dn_a$ (n_a is moles of added alkanol), can be derived by differentiating V in Eq. 6 with C_a at a constant C_d and n_w , in such a simple form as

$$V_a = \Delta V \cdot J + V_{af} \quad (7)$$

where $\Delta V = V_x - V_{af} - V_{df}$, indicating the volume difference on formation of 1 mol of complex, independent of K . The relation represents that V_a is a linear function of J . As a result, the regressive analysis for the linear relation between the measured V_a and the calculated J from Eqs. 4 and 5 including K as an adjustable parameter, at each C_a and C_d , allows the estimation of K . The

obtained linear relation provides ΔV (slope) and V_{af} (intercept), too. These values of K , ΔV , and V_{af} are listed in Table 1. It is noticeable that V_{af} (calculated value) is in good agreement with V_{aw} (measured value) in each system, which proves the validity of the present analysis for K . The calculated V_a by using these estimated values is shown in Fig. 1 by the solid line which is in consistent with the experimental V_a values.

Volume change on complex formation, ΔV

The present analysis gives a significant quantity, ΔV , given in Eq. 7. The value of ΔV is negative (volume decrease) for α -CD, and positive (volume increase) for β -CD, as seen in Table 1, which is also seen in Fig. 1. The ΔV is worthwhile for examining the complex formation mechanism from some different aspects.

The first is based on the geometric dissolution model. Generally, there are two models related to the dissolution of a solute in a solvent, "interstitial" and "substitutional" dissolution models. According to the former model, the PMV of a solute is lower than its molar volume, and to the latter, it is higher. The negative ΔV for α -CD is consistent with the "interstitial" model and implies that the guest alkanol is inserted into a rigid vacant cavity, in line with the generally accepted inclusion model of CD complex formation. In contrast, the unexpected, positive ΔV for β -CD suggests that, consistent with the "substitutional" model, the guest molecule expands the CD cavity on inclusion. The interpretation means that in uncomplexed state in water, the cavity structure is flexible and collapsed, different from the well-known rigid open structure in solid state. According to Nomura et al. [5], the apparent molar adiabatic compressibility of α -, β -, and γ -CD in water is considerably larger than that of glucose and maltose, and they concluded that the cyclic structure of CD is fairly flexible in solution. The flexibility must participate in the present ternary systems. If the cavity of α -CD is not rigid as described above but flexible, the negative ΔV can be attributed to its constriction caused by van der Waals attractive force between the cavity and the guest molecules, closely fitting to each other in the complex.

The second viewpoint involves the hydration and the hydrogen-bonding in the complex formation. In the solid state, CD bears some characteristic hydrated water molecules. Manabe et al. [15] determined the PMV of water (V_{H_2O}) hydrated in solid hydrate of α -, β -, and γ -CD at 298.2 K as a function of molar ratio (R) of water to CD. The determination of V_{H_2O} was made by the similar dilatometry as in the present study, i.e., water was successively injected into a dilatometer in which the absolutely dehydrated CD powder was immersed in dodecane. For each CD, V_{H_2O} was lower than the molar

volume of water and increased stepwise in four steps in the powder state of CD, which indicates the existence of four kinds of characteristic hydrated water, as cited in Table 2 for α - and β -CD. The X-ray analysis for solid hydrate of α -CD evidenced that two water molecules are fitted in the cavity [17, 18]. These two water molecules correspond to those at two lowest ratios, $R_1=1$ and $R_2=2$ for each CD. The other water at higher R_i are supposed to hydrate with OH groups on the periphery of CD cavity.

The values of $V_{H_2O_1}$ and $V_{H_2O_2}$ in Table 2 can be applied to examine the calculations for the contribution to ΔV at 298.2 K. It is considered that the complex formation consists of two steps; first, the two water molecules ($V_{H_2O_1}$ and $V_{H_2O_2}$) are expelled from the cavity to become free water (molar volume, $18.07 \text{ cm}^3 \text{ mol}^{-1}$), and second, a hydrophobic moiety of alkanol is introduced in the vacant cavity. In the first step, these expelled water molecules cause the volume increases by $27.79 (=2 \cdot 18.07 - 2.83 - 5.52)$ and $28.48 (=2 \cdot 18.07 - 2.54 - 5.12) \text{ cm}^3 \text{ mol}^{-1}$ for α -, and β -CD, respectively. If more than two water molecules are fitted in the cavity, in the aqueous solution, the volume increases remarkably. In the second step, tentative calculations can be made from the viewpoint of the hydrophobic bond formation between host and guest in the cavity. Heptanol is taken as a guest, and the molecule is regarded to consist of hydrophobic portion (terminal CH_3 group and the three CH_2 groups adjacent to the CH_3 group) and hydrophilic one (the three CH_2 groups adjacent to the OH group and the OH one). Let us suppose the process that only the hydrophobic portion transfers from aqueous environment to the cavity. Then the residual polar portion remains in some polar environment, such as either in water or in the periphery of cavity. Here, the following PMV value of each group can be assigned for the examining calculation: 19.06 [19] and $32.7 \text{ cm}^3 \text{ mol}^{-1}$ [20] for CH_3 , and 15.76 [16] and 16.96 [16] $\text{cm}^3 \text{ mol}^{-1}$ for CH_2 , in aqueous and hydrophobic media, respectively. As a result, the transfer of the hydrophobic tail in heptanol leads to the volume increase by $17.24 (=32.7 - 19.06 + 3 \cdot (16.96 - 15.76)) \text{ cm}^3 \text{ mol}^{-1}$ for each CD, without any volumetric contribution from the polar portion. After all, the total volume increment in the two steps attains

to $45.03 (=17.24 + 27.79)$ and $45.72 (=17.24 + 28.48) \text{ cm}^3 \text{ mol}^{-1}$ for α - and β -CD, respectively. The examined value for heptanol is about four times greater than ΔV in β -CD ($12.06 \text{ cm}^3 \text{ mol}^{-1}$), and is opposite in sign in α -CD ($-7.66 \text{ cm}^3 \text{ mol}^{-1}$ in Table 1).

Another extreme condition can be considered as the second step mentioned above. If the cavity is rigid and vacant after water molecule leaving, the effective volume, that is, PMV, of the hydrophobic tail (four carbon-chain) itself of the guest inserted interstitially in the cavity can be considered to vanish away. This is reasonably explained from the fact that the PMV of water hydrating in the matrix of a zeolite, molecular sieves 4A, is substantially zero (M. Manabe and H. Kawamura, unpublished data). In this case, the volume change in the second step is estimated to be $-66.34 (=0 - (19.06 + 3 \cdot 15.76)) \text{ cm}^3 \text{ mol}^{-1}$. Then, overall volume change attains to $-38.55 (= -66.34 + 27.79, \text{ in } \alpha\text{-CD})$ and $-37.86 (= -66.34 + 28.48, \text{ in } \beta\text{-CD}) \text{ cm}^3 \text{ mol}^{-1}$. These values are negative and the value even in α -CD is five times greater in magnitude than the present ΔV .

It is apparent that the volume change estimated through the tentative calculations under some extreme conditions is far from the determined ΔV . In order to reduce the discrepancy, some other factors which relax the volume change must be introduced. A plausible factor is the conformational change of CD molecule in water, that is, collapsing or expanding of cavity to fit in nicely with a guest. Therefore, the significant conclusion is derived that in water, CD cavity is not rigid but flexible, different from the widely accepted solid state model. According to the flexible model, the positive ΔV in β -CD can be attributed to expansion of collapsed CD, and the negative ΔV in α -CD to contraction of cavity caused by van der Waals interaction between host and guest.

Dependence of ΔV on alkyl-chain length (m)

Figure 2 shows that the ΔV as a function of m . For β -CD, the positive ΔV value tends to increase simply with increasing m , representing a consistent effect of elongation of alkyl-chain. As for α -CD, the relations are complicated: the negative ΔV tends to decrease with m at

Table 2 Partial molar volume of crystalline water for α - and β -CD solid hydrate at 298.2 K [15]

CD	R_1	V_{w1} ($\text{cm}^3 \text{ mol}^{-1}$)	R_2	V_{w2} ($\text{cm}^3 \text{ mol}^{-1}$)	R_3	V_{w3} ($\text{cm}^3 \text{ mol}^{-1}$)	R_4	V_{w4} ($\text{cm}^3 \text{ mol}^{-1}$)
α -CD	1	2.83	2	5.52	5.6	9.83	6.7	11.96
β -CD	1	2.54	2	5.12	7.5	12.74	11.0	15.32

R_i is molar ratio (water/CD) representing characteristic hydration number
 $V_{w i}$ is PMV of hydrated water and is constant between R_{i-1} and R_i

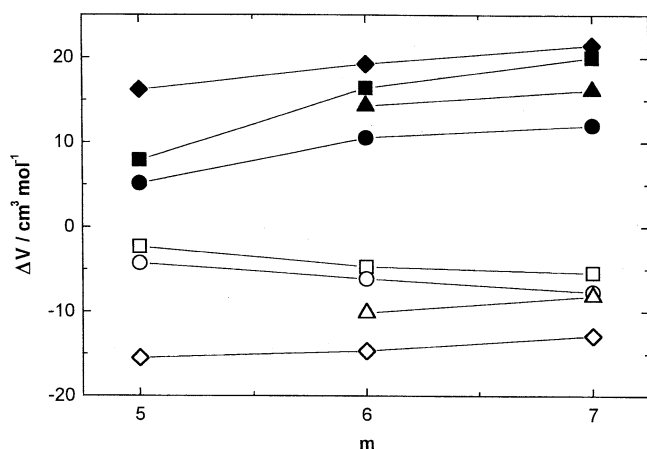


Fig. 2 The relation between PMV change on complex formation and carbon number in alkanols. Temperature/K: 293.2 (*open square*), 298.2 (*open square*), 303.2 (*open circle*), and 308.2 (*open triangle*), in α -CD (*open symbol*) and β -CD (*closed*) solution

lower temperatures but increase at higher temperatures. Restricted to 298.2 K, the dependence can be regarded to be linear for both α - and β -CD, and the extrapolation of the linear relation to $\Delta V=0$ gives $m=3$, approximately. Similar volumetric behavior was observed by Wilson and Verrall [9]. They found that the AMV of homologous ionic surfactants in β -CD solution is larger than in water, and a linear relation between the volume difference and the carbon number (m) of sodium alkyl carboxylates ($m=2, 5-14$) attains to zero at $m=3$, by extrapolating. In addition, the experimentally determined volume difference for the homologue of $m=2$, and the binding constant was observed to be substantially zero. The observation indicates that the short-chain alkanols have very low ability for complex formation than butanol.

On the contrary to the explanation, the complex formation of short-chain alkanols ($m=1-3$) as well as the longer ones ($m=4-8$) with α - and β -CD was determined by a spectroscopic method using an azo dye [21] or phenolphthalein [22] as a probe, and by an NMR technique for self-diffusion measurements [23], whereas no complex formation of the alkanols ($m=1, 2$) with β -CD was observed by the latter method. These results imply that each method has different sensitivity to detect the complex formation. According to the studies [21–23], the relation between $\log(K)$ and m determined by respective methods can be regarded to be linear above $m=3$ and convex upward for the shorter alkanols ($m=1-3$) with exceedingly low K value. The aspects of the break around $m=3$ suggest that the mechanism of complex formation is different from each other, that is, the lower alkanols can form complex without accompanying volume difference in the following manner. When a lower alkanol forms a

complex with a CD, the guest seems to be located in a hydrophilic state such as in the outside (on the periphery) of cavity, rather than in a hydrophobic state in the inside of cavity. Applying the model to the longer-chain alkanols ($m > 3$), it can be mentioned that the polar portion (three CH_2 groups and OH group) of long-chain ones is located in some hydrophilic circumstance whereas the residual hydrophobic portion is accommodated to cause volume increase. The dissolution mechanism is in line with the volumetric behavior on solubilization in surfactant solutions. The PMV of the higher 1-alkanols ($m > 3$) in micellar solution of a surfactant is higher than that in non-micellar one, due to the solubilization, but no volume difference is observed for the lower alkanols ($m < 4$) [13]. The volume difference of a long-chain alkanol is explained to be due to location of some part of alkyl-chain in hydrophobic environment of micelle inside, polar portion of the alkanol molecule being located in the polar environment, such as surface region of micelles, and that for lower alkanols they are located in the latter environment similar to the aqueous one. Accordingly, volumetric data reflects the environment of circumstance of solute molecule.

On the other hand, as for the further long-chain guest of ionic surfactants exceeding $m=8$ [9, 24, 25], the complexation mechanism is reported to be different from the homologues with moderate chain length ($m=4-8$). The chain length ($m > 8$) is too long to be accommodated in a CD cavity. Therefore, it is explained that the hydrophobic moiety including the terminal CH_3 group protrude out from the CD cavity to form 1:2 complex together with another CD molecule. In addition, for 1-alkanols ($m=4-10$) in β -CD, the linear relation of $\log(K)$ with m breaks around $m=8$, [26] in line with the explanation. These aspects lead to a model of inclusion complex that four or five CH_2 groups in the alkyl-chain of some homologues are located in the CD cavity [9, 25, 27]. The tentative calculation of the volume change on complexation described above has been performed on this model.

The slope of the plots in Fig. 2 reflects the contribution of a CH_2 group to ΔV , denoted by $\Delta V(\text{CH}_2)$. The quantity is correlated with the contributions of a CH_2 group to V_x and V_{af} , as Eq. 8 through the definition of ΔV in Eq. 7:

$$\Delta V(\text{CH}_2) = \frac{d(\Delta V)}{dm} = \frac{d(V_x)}{dm} - \frac{d(V_{\text{af}})}{dm} - \frac{d(V_{\text{af}})}{dm} \quad (8)$$

$$= V_x(\text{CH}_2) - V_{\text{af}}(\text{CH}_2)$$

where $d(V_{\text{af}})/dm=0$ is taken into account, V_{af} being the PMV of uncomplexed CD itself. As seen in Tables 1 and 3, the $V_{\text{aw}}(\text{CH}_2)$, i.e., $V_{\text{af}}(\text{CH}_2)$ is not so sensitive to m . Therefore, the complicated dependence of ΔV on m in Fig. 2 can mainly be attributed to that of V_x itself on m .

Partial molar volume of complex, V_x , and its dependence on m

The value of V_x , the PMV of complex itself, can be numerically calculated from $\Delta V (= V_x - V_{af} - V_{df})$ in Eq. 7, if the value of V_{df} is obtained. Only at 298.2 K, the AMV of CD in water at limiting dilution, corresponding to V_{df} has been reported: 601 [4], 611.4 [5], and 615.9 [28] $\text{cm}^3 \text{mol}^{-1}$ for α -CD, and 700.9 [28], 703.8 [5], 704.4 [10], 706.4 [11], 706.5 [6], and 709 [4] $\text{cm}^3 \text{mol}^{-1}$ for β -CD. By averaging these values, V_{df} is taken to be 609.43 (α -CD) and 704.92 $\text{cm}^3 \text{mol}^{-1}$ (β -CD) in order to calculate for V_x shown in Table 3.

The increment of V_x , i.e., $V_x(\text{CH}_2)$, for each CD at 298.2 K is the contribution of CH_2 group. This value can be regarded to be constant within the determination errors. The mean value of $V_x(\text{CH}_2)$ is 14.20 $\text{cm}^3 \text{mol}^{-1}$ for α -CD and 19.34 for β -CD (Fig. 2, Table 3). It should be noted that $V_{aw}(\text{CH}_2)$ (15.90 in Table 3 or 15.76 [16] $\text{cm}^3 \text{mol}^{-1}$) lies between these values: the order of $V_x(\text{CH}_2)$ is that in β -CD > water > α -CD. Hence, for the portion of alkyl-chain located in CD cavity, the interstitial dissolution model and substitutional dissolution model can be applied, in principle, to α -CD and β -CD, respectively. Further, it should be emphasized that $V_x(\text{CH}_2)$ for β -CD is far greater than the volume per CH_2 in an alkyl chain in non-polar media (pure liquid alkanols), 16.96 $\text{cm}^3 \text{mol}^{-1}$ [16], which is consistent with the model that the collapsed cavity of β -CD in water is expanded by the inclusion of alkyl chain. In addition, $V_x(\text{CH}_2)$ for α -CD being smaller than in water is in line with the model of interstitial dissolution or the contraction of cavity by van der Waals interaction.

Dependence of K on m

The relation between $\log(K)$ and m is illustrated in Fig. 3 for α -CD and Fig. 4 for β -CD. For comparison,

Table 3 Derived volumetric data for complex of α - and β -CD with 1-alkanols

T/K	m	V_x ($\text{cm}^3 \text{mol}^{-1}$) ^a		$V_x(\text{CH}_2)$ ($\text{cm}^3 \text{mol}^{-1}$)	$V_{aw}(\text{CH}_2)$ ($\text{cm}^3 \text{mol}^{-1}$) ^d
		α -CD	β -CD		
293.2					15.41
298.2	5	707.61	812.54	14.20 ^b	15.90
298.2	6	721.57	833.77	19.34 ^c	
298.2	7	736.00	851.21		
303.2					16.31
308.2					15.37

^a $V_x = \Delta V + V_{df} + V_{aw}$, where V_{df} ($\text{cm}^3 \text{mol}^{-1}$) = 609.43(α -CD), 704.92(β -CD), see in text

^bFor α -CD

^cFor β -CD

^dCalculated from V_{aw}

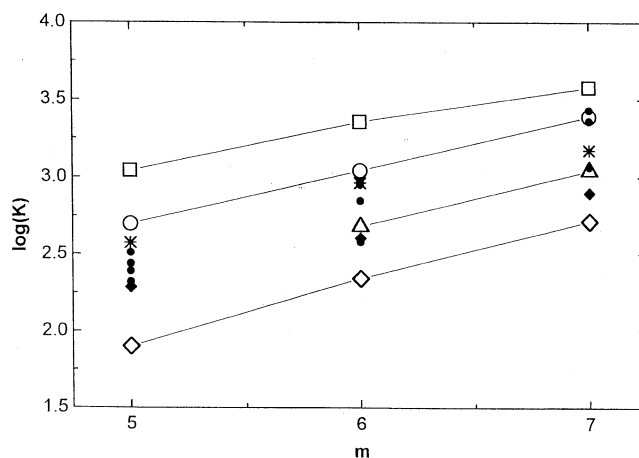


Fig. 3 The relation between binding constant and carbon number in alkanols, in α -CD solution. Temperature/K: 293.2 (open square), 298.2 (open circle), 303.2 (open triangle), and 308.2 (open diamond). Corresponding closed small symbol and the star symbol (288.2 K) indicate literature data in Table 1

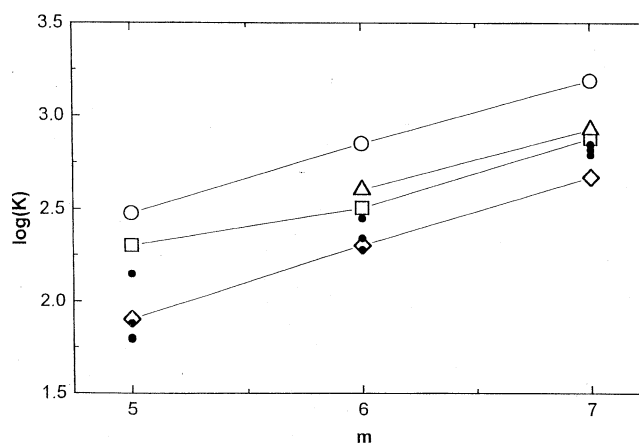


Fig. 4 The relation between binding constant and carbon number in alkanols, in β -CD solution. Temperature/K: 293.2 (open square), 298.2 (open circle), 303.2 (open triangle), and 308.2 (open diamond). Closed small circle indicates literature data at 298.2 K in Table 1

the literature data of K determined by various methods, listed in Table 1, are also plotted, where the data are limited only at 298.2 K except the data in α -CD from Hallen et al. [29]. The present values of K in α -CD are in reasonable agreement with the literature ones (Fig. 3), but in β -CD at 298.2 K, the former is more than twice greater than the latter for each alkanol (Fig. 4). The discrepancy might be attributed to the difference of determination methods each of which has different sensitivity to different characteristic of complexation.

These figures represent that $\log(K)$ increases almost linearly with increasing m , in all systems studied. The free energy change on complex formation can be cal-

culated as $\Delta G^\circ = -RT \ln(K)$, where R and T are gas constant and absolute temperature, respectively. Then the CH_2 group contribution to ΔG° expressed as $\Delta G^\circ(\text{CH}_2)$ can be estimated from the slope of $\log(K)-m$ plot to be around $-0.79RT$ for both α - and β -CD at the temperatures studied. At 298.2 K, the values of $\Delta G^\circ(\text{CH}_2)$ calculated between $m=4$ and 8 from the literature data can be compared as follows: in $-RT$ unit, 1.07 [21], 1.31 [23], in α -CD, and 1.15 [21], 1.06 [22], 0.52 [23], 1.14 [26] in β -CD. These values including present one gives the averaged value as $-0.98RT$. This is numerically in fairly good agreement with $\Delta G^\circ(\text{CH}_2)$ involving hydrophobic interaction of transfer of CH_2 group from water to micelle ($-1.0RT$) [13] and a little smaller in magnitude than that from water to dodecane ($-1.4RT$) [30]. The comparison of $\Delta G^\circ(\text{CH}_2)$ values allows us to evaluate the hydrophobicity of cavity inside to be the extent of micelles of surfactants.

Temperature dependence of K

The van't Hoff plot of $\log(K)$ versus $1/T$ allows us to estimate the standard enthalpy change for complex formation, ΔH° , and obtained values are listed in Table 4, in comparison with the literature data [21, 29, 31–33]. These negative values imply that the complex formation is exothermic. These values are nearly ten times greater in magnitude than reported ones determined calorimetrically in the corresponding systems of α -CD [21, 29, 31–33], and are even opposite in sign in β -CD [21, 32]. The reason of such remarkable disagreement might be that the volume change with complexation are not sensitive enough to determine accurate binding constant, or the linear relation of the van't Hoff plot is not valid because the heat capacity cannot be ignored [29]. Therefore, regrettably, further discussion about the temperature dependence is unfruitful.

Table 4 Standard change of enthalpy for complex formation of α - and β -CD with 1-alkanols at 298.2 K

m	ΔH° (kJ mol ⁻¹)			
	[α -CD]		[β -CD]	
	This work	Lit.	This work	Lit.
5	-132.4 ^a	-16 ^b , -14.92 ^c , -11.8 ^d , -14.8 ^f	-101.0	4.6 ^b
6	-117.2 ^a	-19 ^b , -18.20 ^c , -17.5 ^d , -29.1 ^e , -17.2 ^f	-96.73	0.4 ^b , 0.6 ^c
7	-101.5 ^a	-22.8 ^c	-91.16	

^aCalculated from K values except those at 293.15 K

^bRef. [21]

^cRef. [29]

^dRef. [31]

^eRef. [32]

^fRef. [33]

Conclusion

The V_a of 1-alkanols ($m=5, 6, 7$) in the solution of α - and β -CD ($C_d = 5.00 \text{ mmol kg}^{-1}$) was measured between 293.2 and 308.2 K as a function of C_a . It is found that the volume change with complexation is negative for α -CD, and positive for β -CD. The significant volumetric behavior leads to the complex formation model that the CD cavity is flexible in water, not to be rigid in such solid state. The β -CD cavity which is collapsed in water is expanded by the included guest, and the α -CD cavity with open structure is contracted on complexation by the van der Waals interaction.

The C_a dependence of V_a allows us to estimate K as well as the PMV change of complex formation, $\Delta V = V_x - V_{af} - V_{df}$ in addition to the PMV of the complex itself, V_x . The carbon number dependence of respective quantities, K and V_x , suggests that the hydrophobic interaction also participates in the complex formation.

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