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論 文

Enthalpy and Entropy Changes on Molecular Inclusion of 1-Butanol into α- and β-Cyclodextrin Cavities in Aqueous Solutions

Masao Fujisawa[a], Takayoshi Kimura[a] and Sadao Takagi[a]*

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Enthalpy of dilution of dilute aqueous solution of 1-butanol and those of transfer of 1-butanol from dilute aqueous solution to dilute aqueous α- and β-cyclodextrin solutions have been determined by microcalorimetry. The molar enthalpies, entropies, and Gibbs energies of inclusion as well as the equilibrium constants of 1 : 1 inclusion-complex formation and ratios of included 1-butanol at infinite dilution at 298.15 K have also been determined. The dependences of enthalpies and entropies of inclusion on the number of carbon atoms in the alkyl radicals of alcohol molecules are discussed.

1. Introduction

Mechanisms of molecular recognition and discrimination in the processes of many chemical reactions, including biochemical reactions in living bodies, may be understood by elucidating the stereospecific interactions between contacting surfaces of colliding molecules in solutions. To clarify the mechanisms, the present authors and others[1-7] have determined basic thermodynamic functions concerning the molecular recognition and discrimination quantitatively by precise microcalorimetry.

In the paper, the thermodynamic functions of molecular inclusion of 1-butanol (simply "butanol" will be used in this text, hereafter) into α- and β-cyclodextrin (CD) cavities in aqueous solutions are described in order to judge the existence of any correlation between the molar enthalpy and entropy of inclusion and the number of carbon atoms in linear chain aliphatic alcohols, namely, the number of methyl and methylene radicals.

2. Experimental

Materials

1-Butanol (Merck, Uvasol) was refluxed for 24 h in a 1 m column filled with Helipack® over the molecular sieves® 4A which had been activated by heating at 423 K for 12 h or more under the reduced pressure of $10^{-2} \sim 10^{-3}$ Pa. Then, it was fractionally distilled through the column at high reflux ratios. Purity of the distillate was found to be higher than 99.9 mass per cent, excluding water, by the use of GLC (Yanagimoto, model G180FP) and the water content of final product of butanol was smaller than 0.01 mole per cent. The latter was obtained by the coulometric Karl-Fischer's method on a Mitsubishi Moisture Meter, model CA-02.

Detailed procedures of careful purification used for the α-CD,[1] β-CD,[2] water,[8] and mercury[9] were described earlier. All solutions were prepared by mass.

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* To whom correspondence should be addressed.

[a] Depertment of Chemistry, Faculty of Science and Technology, Kinki University, 3-4-1 Kowakae, Higashi-osaka 577, Japan

Apparatus and Procedures

The measurements of enthalpies of mixing of aqueous butanol solutions and aqueous CD solutions and those of dilution of aqueous butanol solutions were carried out at 298.15 K on a rocking twin-microcalorimeter of a heat-conduction type, laboratory designation RMC-III, which had been improved by minor modification of the microcalorimeter so far used by the present authors, RMC-II.[1-5] A matched pair of Melcore CP 1.4-71-10 *p-n* semiconductor thermopiles was mounted in place of original ones. A Keithley model 148 nanovoltmeter was used as a d.c. amplifier of the difference in *e. m. f.* of the thermopiles between the measuring vessel and the reference one. The whole apparatus was installed in a temperature-controlled room at ±0.1 K and the thermostatted water at (298.15±0.0005) K was circulated around a large aluminium block (heat sink) of the microcalorimeter.

About 3.0 g of aqueous CD solution and about 0.75 g of aquenous butanol solution was loaded into a mixing vessel filled with mercury from weighed syringes fitted with suitably bent stainless-steel needles. In dilution measurements, about 3.0 g of water and about 0.75 g of dilute aqueous solution of butanol were loaded. Compartments of a similar mixing vessel used for reference were loaded with about 3.0 g and 0.75g of water, respectively.

Details of procedures for measurements of enthalpies are similar to those described elsewhere.[9] Rocking was, however, carried out ten times in each run and the mercury used in the present work was purified and freshly distilled in vacuo before each measurement.

3. Results and Discussions

Enthalpy of dilution

The experimental values of the enthalpy changes on diluting the dilute aqueous butanol solutions ranging from 1.1×10^{-3} to 4.3×10^{-3} in mole fraction to final solutions ranging from 2.0×10^{-4} to 7.8×10^{-4} at 298.15 K under the atmospheric pressure are given in Table 1. Here n_3 denotes the amount of butanol in the solutions and x_i and x_f are the mole fractions before and after the dilution, respectively.

Table 1　Experimental enthalpies of dilution $\Delta_{dil}H$ of dilute aqueous 1-butanol solutions with water at 298.15 K

$10^4 n_3$/mol	$10^3 x_i$	$10^4 x_f$	$-\Delta_{dil}H$/mJ	$\delta(\Delta_{dil}H)$/mJ
1.675	4.325	7.764	33.0	0.7
1.438	3.552	6.596	24.3	-1.7
1.170	2.714	5.375	12.7	0.4
1.144	2.363	4.660	8.19	1.8
1.038	2.657	4.740	12.1	-0.5
0.4272	1.088	2.037	2.75	-1.0

Table 2　Parameters *a* and *b* in Eqn. (2) and the calculated standard deviation s_f of the fit

	a/kJ·mol^{-1}	b/kJ·mol^{-1}	s_f/mJ
1-Butanol	-42.5	-2802	1.6

The results were fitted to Eqn. (1) by the least-squares calculation.

$$\Delta_{dil}H = an_3(x_i - x_f) + bn_3(x_i^2 - x_f^2) + cn_3(x_i^3 - x_f^3) \qquad (1)$$

Both of Eqn. (1) and the equation having only the first and second terms in Eqn. (1) represented the experimental results within experimental errors. Thus, two parameters a and *b* are listed in Table 2 as well as the calculated standard deviation of the fit. The last column $\delta(\Delta_{dil}H)$ of Table 1 shows the differences in $\Delta_{dil}H$ between the experimental results and the corresponding smoothed values.

The molar enthalpy of dilution of aqueous butanol solution having a mole fraction *x* to infinite dilution can be obtained by Eqn. (2) with the parameters *a* and *b* given in Table 2.

$$\Delta_{dil}{}^{\infty}H_m = ax + bx^2$$

Comparisons of the calculated molar enthalpies of dilution with the experimental ones are illustrated in Fig. 1, where vertical lines show the molar values

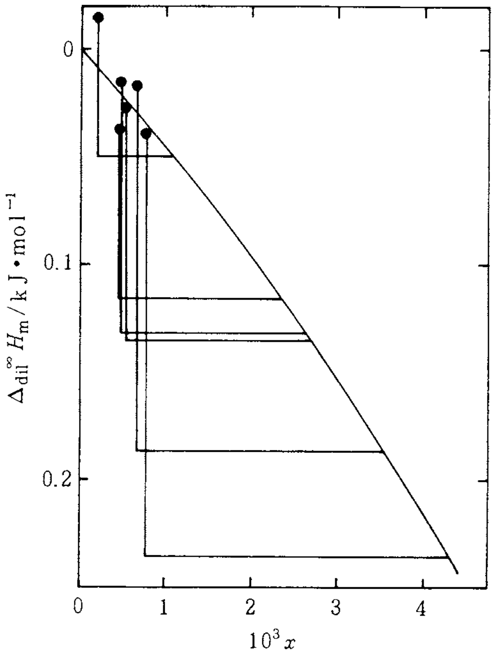

Fig. 1 Comparison of the experimental molar enthalpies of dilution with the smoothed values for aqueous 1-butanol mixture at 298.15K. Solid curve represents the molar enthalpy of dilution to infinite dilution.

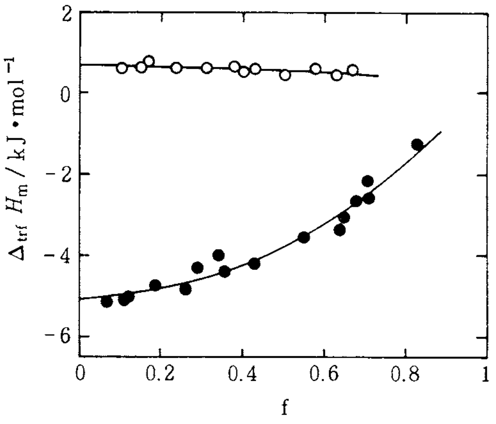

Fig. 2 Molar enthalpies of transfer $\Delta_{trf}H_m$ of 1-butanol from aqueous to aqueous α-CD (●) and β-CD (○) solutions at 298.15 K as a function of $f = n_3/(n_2+n_3)$. Curves represent the smoothed values for α-CD ($z_{mean}=4947$) and β-CD ($z_{mean}=4945$).

Table 3 Experimental enthalpies of mixing $\Delta_{mix}H$ and molar enthalpies of transfer $\Delta_{trf}H_m$ of 1-butanol from dilute aqueous solutions to dilute α-cyclodextrin solutions at 298.15 K

f[a]	$10^2 n_1'$/mol	$10^2 n_1''$/mol	$10^5 n_2$/mol	$10^5 n_3$/mol	$\Delta_{mix}H$/mJ	$\Delta_{trf}H_m$/kJ•mol^{-1}	$\delta(\Delta_{trf}H_m)$/kJ•mol^{-1}
			$H_2O(1) + \alpha$-CD(2) + 1-BuOH(3)				
0.0678_5	16.643	4.104	4.355	0.3170	-15.9	-5.16	-0.12
0.1127_2	17.158	3.487	3.955	0.5024	-25.4	-5.12	-0.14
0.1211_7	16.916	4.026	4.229	0.5831	-29.0	-5.04	-0.08
0.1856_7	15.913	4.169	4.001	0.9122	-43.2	-4.77	0.08
0.2607_9	16.597	3.996	4.056	1.431	-69.5	-4.87	-0.18
0.2916_6	17.003	3.969	4.343	1.788	-76.9	-4.31	0.31
0.3415_7	16.883	4.133	4.184	2.170	-86.9	-4.01	0.47
0.3552_4	15.497	3.742	3.741	2.061	-91.0	-4.41	0.02
0.4296_1	16.412	3.820	4.200	3.164	-133.9	-4.22	-0.05
0.5489_1	16.407	4.012	4.202	5.113	-182.5	-3.53	0.05
0.6365_3	17.255	3.813	4.416	7.733	-268.7	-3.40	-0.40
0.6476_5	17.821	4.559	4.392	8.072	-252.4	-3.07	-0.13
0.6746_9	15.814	3.954	4.191	8.691	-238.8	-2.67	0.04
0.7080_0	18.150	4.379	4.498	10.91	-243.8	-2.14	0.32
0.7087_8	19.163	4.019	4.626	11.26	-300.9	-2.56	-0.10
0.8258_9	18.170	4.304	4.643	22.02	-326.6	-1.24	0.21

[a] The mole fraction $f = n_3/(n_2+n_3)$.

of the experimental enthalpies of dilution, $\Delta_{dil}H/n_3$, from x_i to x_f. The smoothed values are calculated by Eqn. (3).

$$\Delta_{dil}H_m = \Delta_{dil}{}^{\infty}H_m(x_i) - \Delta_{dil}{}^{\infty}H(x_f) \qquad (3)$$

Enthalpy of transfer

The experimental enthalpies of mixing and the related quantities are summarised in Tables 3 and 4. The average values of $z = (n_1' + n_1'')/n_2$[1-4]were 4947 ± 150 and 4995 ± 537, respectively, for α-CD and β-CD. The experimental enthalpies of transfer of butanol from aqueous to aqueous α- or β-CD solutions determined by Eqn. (4)[1-4]are also summarised

$$\Delta_{trf}H = \Delta_{mix}H - \Delta_{dil}H_{12} - \Delta_{dil}H_{13} \qquad (4)$$

in the seventh column of Table 3 or 4 and are

Table 4　Experimental enthalpies of mixing $\Delta_{\mathrm{mix}}H$ and molar enthalpies of transfer $\Delta_{\mathrm{trf}}H_{\mathrm{m}}$ of 1-butanol from dilute aqueous solutions to dilute β cyclodextrin solutions at 298.15 K

f[a]	$10^2n_1'$ / mol	$10^2n_1''$ / mol	10^5n_2 / mol	10^5n_3 / mol	$\Delta_{\mathrm{mix}}H$ / mJ	$\Delta_{\mathrm{trf}}H_{\mathrm{m}}$ / kJ•mol^{-1}	$\delta(\Delta_{\mathrm{trf}}H_{\mathrm{m}})$ / kJ•mol^{-1}
			$H_2O(1) + \beta$-CD(2) + 1-BuOH(3)				
0.0981_6	16.545	4.047	4.321	0.4703	2.80	0.599	-0.06
0.1440_0	16.397	4.162	4.793	0.8064	4.90	0.614	-0.03
0.1668_9	16.238	4.875	4.875	0.9767	7.15	0.739	0.09
0.2329_2	16.713	3.922	3.231	0.9812	5.96	0.616	-0.02
0.3058_8	15.952	4.047	4.081	1.798	10.65	0.608	-0.01
0.3738_1	17.248	4.095	4.194	2.503	15.31	0.634	0.29
0.4007_5	16.448	3.740	3.945	2.638	13.19	0.526	-0.07
0.4260_2	16.583	3.808	4.250	3.154	18.10	0.604	0.02
0.5071_7	16.429	4.338	3.878	3.990	15.97	0.433	-0.13
0.5759_3	16.816	3.939	4.217	5.727	31.45	0.605	0.07
0.6268_8	16.389	3.765	3.930	6.602	25.33	0.452	-0.06
0.6638_2	17.180	3.773	4.318	8.527	41.96	0.584	0.10

[a] The mole fraction $f = n_3/(n_2 + n_3)$.

Table 5　Equilibrium constants for the formation of 1 : 1 inclusion complexes, the limiting molar enthalpies of transfer of 1-butanol, and the limiting molar ratios y_{max} of 1-butanol included at 298.15 K

system	$\log_{10}K$	$\Delta_{\mathrm{trf}}H^{\infty}_{\mathrm{m}}$ / kJ•mol^{-1}	y_{max}
1-BuOH + α-CD	3.96	-5.13	0.652
1-BuOH + β-CD	4.08	0.67	0.224

plotted in Fig. 2 against the mole fraction of butanol, $f = n_3/(n_2 + n_3)$, where the mole fraction of water is omitted for convenience. The amount of water is taken into account in the parameter z.[1-3] In the calculations, the enthalpies of dilution of aqueous butanol solutions, $\Delta_{\mathrm{dil}}H_{13}$, were determined by Eqns. (2) and (3) with the parameters a and b given in Table 2. Those of α-CD solution[6] and β-CD solution,[2] $\Delta_{\mathrm{dil}}H_{12}$, were obtained from our earlier papers.

Table 6　The changes of thermodynamic functions on 1 : 1 inclusion of an alcohol in aqueous solutions at 298.15 K

Alcohol	$\Delta_{\mathrm{inc}}H_{\mathrm{m}}$ / kJ•mol^{-1}	$\Delta_{\mathrm{inc}}G_{\mathrm{m}}$ / kJ•mol^{-1}	$-T\Delta_{\mathrm{inc}}S$ / kJ•mol^{-1}	$\Delta_{\mathrm{inc}}S_{\mathrm{m}}$ / J•(K•mol)$^{-1}$
	α-Cyclodextrin			
1-Propanol[a]	-6.6	-17.8	-11.2	37.5
1-Butanol	-7.9	-22.6	-14.7	49.5
1-Pentanol[a]	-13.9	-24.4	-10.4	34.9
2-Propanol[a]	-0.4	-19.2	-18.8	63.0
1,3-Butanediol[b]	-1.3	-24.0	-22.7	76.1
Cyclohexanol[a]	-7.9	-23.8	-15.9	53.3
	β-Cyclodextrin			
1-Propanol[a]	1.9	-17.5	-19.4	65.0
1-Butanol	3.0	-18.0	-21.0	70.5
1-Pentanol[a]	2.2	-22.6	-24.8	83.2
2-Propanol[a]	1.2	-19.7	-20.9	70.1
1,3-Butanediol[b]	-1.4	-23.3	-21.9	73.4
Cyclohexanol[a]	-7.0	-24.9	-17.9	60.1

[a] Cited from reference 4. [b] Cited from reference 6.

From those experimental values of $\Delta_{\mathrm{trf}}H_{\mathrm{m}}$ as a function of f and z, the equilibrium contants K of 1 : 1 inclusion-complex formation, limiting molar enthalpies of transfer $\Delta_{\mathrm{trf}}H^{\infty}_{\mathrm{m}}$ and limiting ratios of butanol included over the total butanol in the system y_{max} at infinite dilution were determined by the least-squares calculation of Eqn. (9) in the paper III of this series.[3] These quantities thus determined are summarised in Table 5. The smoothed values of $\Delta_{\mathrm{trf}}H_{\mathrm{m}}$ are drawn as functions of f for the cases having mean values of z in Fig. 2.

Enthalpy and entropy of inclusion

From the thermodynamic functions given inTable 5, the molar enthalpies, molar Gibbs energies and molar entropies of inclusion of butanol into α-CD and β-CD in aqueous solutions at 298.15 K under atmospheric pressure were determined by Eqns. (5) – (7) and are summarised in Table 6, as well as the reported values for the sake of comparison.[4,6]

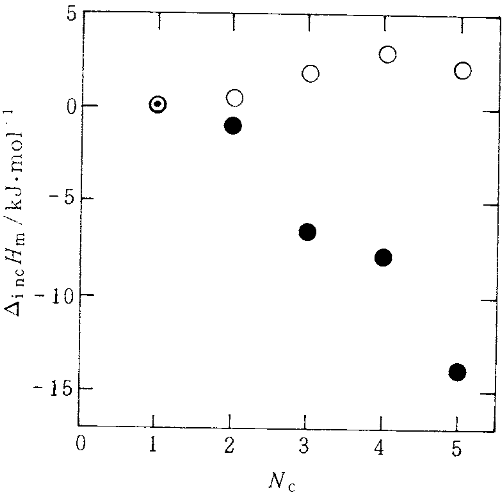

Fig. 3 Molar enthalpies of inclusion $\Delta_{inc}H_m$ of linear aliphatic alcohols into α-CD (●) and β-CD (○) cavities in aqueous solutions at 298.15 K plotted against the number of carbon atoms N_c in the alcohols. The values for alcohols except 1-butanol were cited from references.[3-4]

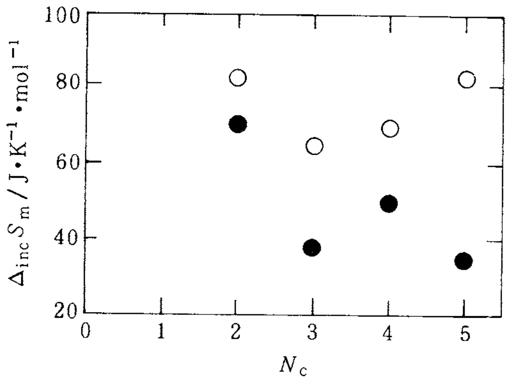

Fig. 4 Molar entropies of inclusion $\Delta_{inc}S_m$ plotted against the number of carbon atoms in the alcohol molecules at 298.15 K : ●, α-CD, ○, β-CD.

$$\Delta_{inc}H_m = \Delta_{trf}H^{\circ}{}_m / y_{max} \quad (5)$$

$$\Delta_{inc}G_m = -RT\ln K \quad (6)$$

$$\Delta_{inc}S_m = \frac{\Delta_{inc}H_m - \Delta_{inc}G_m}{T} \quad (7)$$

The enthalpies of inclusion of butanol are negative for α-CD and positive for β-CD in accord with other aliphatic alcohols listed in Table 6. Fig. 3 shows that the enthalpies $\Delta_{inc}H_m$ depend upon the odd and even numbers of carbon atoms N_c in alcohol molecules and in each series of odd and even numbers linear correlation between $\Delta_{inc}H_m$ and N_c seems to exist which may be nearly parallel each other.

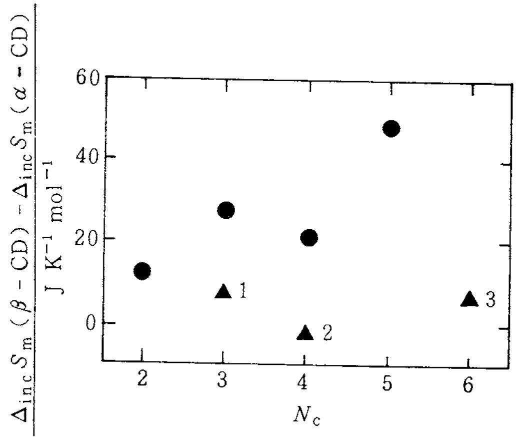

Fig. 5 Difference of the entropies of inclusion $\Delta_{inc}S_m$ of alcohols in β-CD and α-CD cavities: ●, n-alkane-1-ol; 1, 2-propanol; 2, 1,3-butanediol; 3, cyclohexanol.

The molar entropies of inclusion $\Delta_{inc}S_m$ of butanol to α-CD and β-CD cavities are positive and large in accord with other alcohols given. There is no definite correlation between $\Delta_{inc}S_m$ and the number of carbon atoms N_c in alchol molecules as shown in Fig. 4. However, the molar entropies of inclusion seem to depend on even or odd N_c for both CD's. Fig. 5 shows the difference of the entropy of inclusion of the same alcohol between β-CD and α-CD cavities. To explain the dependence of the above difference on the number of carbon atoms, additional information about the behaviour of water molecules remaining in the β-CD cavities with an alcohol moecule is required, because the difference becomes larger with the increase of N_c for the linear aliphatic alcohols.

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要　旨

1―ブタノール希薄水溶液の希釈エンタルピーと1―ブタノールを希薄水溶液中からα-およびβシクロデキストリンの希薄水溶液中へ移行した際のエンタルピー変化をミクロカロリメトリーにより決定した。さらに，298.15Kでの無限希釈における1：1包接化合物形成の平衡定数，1―ブタノールの被包接化率，包接化エンタルピー，包接化エントロピー，包接化Gibbsエネルギーを決定した。α-シクロデキストリン空洞への包接に対しては，モル包接化エンタルピーはメタノールからペンタノールまでの直鎖アルコールでアルコールの炭素原子数の奇偶に依存すること，また奇数あるいは偶数の炭素原子を有するアルコールについて，それぞれの系列でモル包接化エンタルピーが炭素原子数の増加とともに等しい割合で直線的に減少することを見出した。