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Enthalpy and entropy changes on molecular inclusion of 1,4-butanediol into α- and β-cyclodextrin cavities in aqueous solutions

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Abstract

To determine the enthalpies and entropies of inclusion, enthalpies of dilution of dilute aqueous 1,4-butanediol (BD) solutions and those of transfer of 1,4-BD from aqueous to aqueous α- or β-cyclodextrin (CD) solutions have been determined by microcalorimetry at various mole fractions at 298.15 K. Enthalpies of inclusion of 1,4-BD molecules into α- and β-CD cavities are determined, whose values are exothermic and small. However, stabilisation of gaseous 1,4-BD molecules in the CD cavities is large. 1,4-BD molecules must change their conformations to make the closest contacts with the atoms on the wall of α-CD cavities or those on the wall of β-CD cavities and the remaining water molecules in β-CD cavities. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Molecular recognition; 1,4-Butanediol; Cyclodextrin; Enthalpy of inclusion; Entropy of inclusion

1. Introduction

Cyclodextrin (CD) molecules include many kinds of guest molecules in their molecular cavities recognising the difference in structure of those in aqueous solutions. The changes of thermodynamic functions on molecular inclusion of monohydric alcohols and 1,3- and meso-2,3-butanediols (BD) [1–9] into α- and β-cyclodextrin (CD) cavities in aqueous solutions have been determined systematically by the present authors by precise microcalorimetry, in order to clarify the mechanisms of molecular recognition and discrimination in aqueous solutions.

In this paper, the thermodynamic functions of molecular inclusion of 1,4-BD into α- and β-CD cavities are described to clarify the difference between 1,4-BD and other alcohols.

2. Experimental

2.1. Materials

1,4-BD (Tokyo Kasei G.R.grade) was dried with K_2CO_3, keeping them in contact with each other for two months and fractionally distilled under reduced pressure through a 1 m Helipack column. It was fractionally distilled further through a spinning-band column at high reflux ratios passing dry N_2 gas under

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Table 1
Experimental enthalpies of dilution $\Delta_{\text{dil}}H$ of dilute aqueous 1,4-butanediol solutions with water at 298.15 K

10^4n_3 (mol)	10^4x_i	10^4x_f	$-\Delta_{\text{dil}}H$ (mJ)	$\delta(\Delta_{\text{dil}}H)$[a] (mJ)
1.1046	2.817	5.401	17.2	−0.2
0.8531	2.195	4.262	10.8	0.9
0.7851	2.090	3.923	11.9	−1.3
0.7398	1.936	3.610	8.6_7	1.0
0.7238	1.863	3.636	8.4_8	0.6
0.6931	1.832	3.435	8.8_9	−0.2
0.6292	1.569	3.098	7.6_8	−0.7
0.5603	1.459	2.716	6.6_1	−0.6
0.2542	0.650	1.269	0.98	0.4

[a] Difference from the smoothed values.

the reduced pressure of 0.4 kPa over freshly activated molecular sieves 4A, after the total reflux for 24 h [6]. The coulometric Karl–Fischer's method on a Mitsubishi Moisture Meter model CA-02 gave the water content of the 1,4-BD to be 0.002 mass percent.

Details of the careful purification used for the α-CD [1], β-CD [2], water [10] and mercury [11] were described earlier. The mercury used was freshly distilled in vacuo before each measurement. All solutions were prepared by mass. The aqueous 1,4-BD mixtures prepared were stirred for 10 min at room temperature on a magnetic stirrer. Then, they were stirred vigorously for ca. 15 min at room temperature with a supersonic washer (Taga Electric model UW-25, output frequency: 38 kHz, 45 W) before changing them into mixing vessels to make sure that the mixtures are easy to reach equilibrium in holding periods for measurements. Takagi et al. [12] already found that the mixtures of water and 1,4-BD required a lot of time to reach equilibria at room temperatures. This was presented before the informal meeting held at the seventh IUPAC Conference on Chemical Thermodynamics, London in 1982 and some other symposiums.

2.2. Apparatus and procedures

A rocking twin-microcalorimeter of a heat-conduction type, laboratory designation RMCIII[1] [6,7], was used for the determination of enthalpies of dilution and transfer. All the measurements were carried out at 298.15 K under the atmospheric pressure. Enthalpy changes were measured automatically with an on-line system described elsewhere [13]. Details of the apparatus and procedures, including the mixing vessels [5], are similar to those described previously [6,7].

3. Results and discussion

3.1. Enthalpy of dilution

The experimental results for the enthalpy changes on diluting the dilute aqueous 1,4-BD solutions ranging from 6.5×10^{-4} to 2.8×10^{-3} in mole fraction to final solutions ranging from 1.3×10^{-4} to 5.4×10^{-4} at 298.15 K under the atmospheric pressure are given in Table 1, where n_3 denotes the amount of 1,4-BD in the solutions and x_i and x_f, respectively, are the mole fractions before and after the dilution.

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

$$\Delta_{\text{dil}}H = an_3(x_\text{i} - x_\text{f}) + bn_3(x_\text{i}^2 - x_\text{f}^2) + \cdots \tag{1}$$

The best-fit values for the parameters in Eq. (1) are listed in Table 2, as well as the calculated standard deviation of the fit s_f. The last column of Table 1 shows

Table 2
Parameters a and b in Eq. (1) and the calculated standard deviation s_f of the fit

	a (kJ mol^{-1})	b (kJ mol^{-1})	s_f (mJ)
1,4-Butanediol	−115.4	14268	0.89

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[1] Rocking conduction microcalorimeter in the third stage of modification [5].

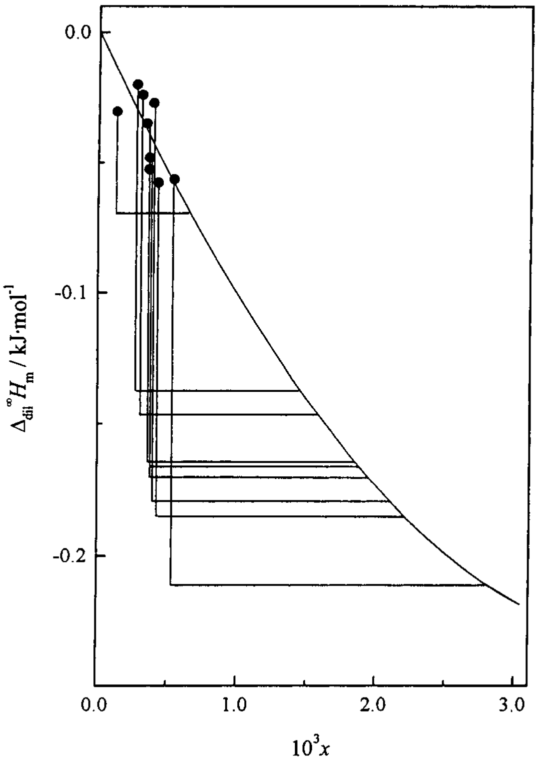

Fig. 1. Molar enthalpies of dilution of dilute aqueous 1,4-butanediol solutions to infinite dilution at 298.15 K plotted against mole fraction x, where the curve represents smoothed values calculated by Eq. (2) with a and b in Table 2. Horizontal lines show the ranges of x diluted and vertical heights represent the values of $\Delta_{dil}H/n_3$ obtained from Table 1.

the differences in $\Delta_{dil}H$ between the experimental results and the corresponding smoothed values.

The molar enthalpy of infinite dilution of aqueous 1,4-BD solution having a mole fraction x to $x=0$ can be obtained by Eq. (2) with the parameters a and b obtained from Eq. (1) and listed in Table 2.

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

Fig. 1 shows the comparison of the smoothed molar enthalpies of dilution with the experimental ones. Here vertical lines represent the molar values of the experimental enthalpies of dilution, $\Delta_{dil}H/n_3$, from x_i to x_f. The smoothed values are obtained from the curve in Fig. 1 by Eq. (3).

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

3.2. Enthalpy of transfer

The experimental enthalpies of mixing and the related quantities are summarised in Table 3. The average values of $z=(n_1'+n_1'')/n_2$ [1–3] were 4919 ± 226 and 6749 ± 1227, respectively, for α-CD and β-CD. The experimental enthalpies of transfer of 1,4-BD from dilute aqueous solutions to dilute aqueous α- or β-CD solutions determined by Eq. (4) [1–4] are also summarised in the last column of Table 3. In the calculation through Eq. (4), the enthalpy of dilution of aqueous 1,4-BD solution,

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

$\Delta_{dil}H_{13}$ was determined by Eqs. (2) and (3) with the parameters given in Table 2. Those of α-CD solution [7] and β-CD solution [2], $\Delta_{dil}H_{12}$, were obtained from our earlier papers.

By the least-squares treatment of the experimental values of $\Delta_{trf}H_m$ as a function of z and the mole fraction of 1,4-BD, $f=n_3/(n_2+n_3)$, according to the Eq. (9) described in the earlier paper of this series [3] limiting molar enthalpies of transfer at infinite dilution, $\Delta_{trf}H_m^{\infty}$ were determined as well as the equilibrium constants K of 1:1 inclusion-complex formation and limiting ratios y_{max} of 1, 4-BD included over the total 1, 4-BD in the systems at infinite dilution. These quantities thus determined are summarised in Table 4. The smoothed values of $\Delta_{trf}H_m$ for the mean values of z are drawn in Fig. 2 against the mole fraction f.

In Fig. 2, molar enthalpies of transfer of other alcohols determined by a series of our systematic studies [1–4,6–7] are also plotted against their mole fractions f, for the sake of comparison. The transfer of BD's evolves only small heats for both α- and β-CD cavities, although their molecular sizes are larger than those of propanol and butanol. Enthalpic stabilisation accompanied by the transfers of 1,4-BD are slightly larger than that of 1,3-BD.

3.3. Enthalpy and entropy of inclusion

From the thermodynamic functions listed in Table 4, the molar enthalpies, molar Gibbs energies and molar entropies of inclusion of 1,4-BD at infinite dilution of 1,4-BD into α-CD and β-CD cavities in very dilute aqueous solutions (cf. z) at 298.15 K under the atmospheric pressure were determined and are summarised

Table 3
Experimental enthalpies of mixing $\Delta_{\mathrm{mix}}H$ and molar enthalpies of transfer $\Delta_{\mathrm{trf}}H_m$ of 1,4-BD from dilute aqueous solutions to dilute aqueous α- or β-cyclodextrin solutions at 298.15 K, where n'_1, n''_2, and n_3 represent, respectively, amounts of water in the CD solution, amounts of water in the 1,4-BD solution, amounts of cyclodextrin (CD) in the aqueous solution and amounts of 1,4-BD in the aqueous solution

f[a]	$10^2 n'_1$ (mol)	$10^2 n''_1$ (mol)	$10^5 n_2$ (mol)	$10^5 n_3$ (mol)	$\Delta_{\mathrm{mix}}H$ (mJ)	$\Delta_{\mathrm{trf}}H_{\mathrm{m}}$ (kJ mol^{-1})
$H_2O(1)+\alpha\text{-}CD(2)+1,4\text{-}BD(3)$						
0.1417_1	16.189	3.446	4.186	0.6912	−10.7	−1.59
0.1537_2	16.323	3.865	4.031	0.7321	−10.8	−1.52
0.2366_7	15.283	3.993	3.804	1.179	−15.7	−1.34
0.2796_2	16.078	3.882	3.838	1.490	−18.1	−1.21
0.3959_6	16.233	3.431	4.014	2.632	−24.3	−0.873
0.5300_4	16.571	4.108	4.118	4.644	−45.7	−0.906
0.5945_2	16.036	4.011	4.028	5.906	−54.9	−0.831
0.6917_5	16.350	4.098	4.552	10.216	−82.7	−0.670
$H_2O(1)+\beta\text{-}CD(2)+1,4\text{-}BD(3)$						
0.1292_4	16.226	4.187	2.785	0.4133	−4.39	−1.05
0.1448_5	16.190	4.187	2.807	0.4754	−4.62	−0.962
0.1826_7	16.098	3.778	3.957	0.8843	−6.83	−0.751
0.1833_1	16.194	4.212	2.886	0.6477	−5.48	−0.832
0.2211_6	16.734	3.870	2.572	0.7304	−4.37	−0.581
0.3072_4	16.254	4.054	2.831	1.256	−8.70	−0.666
0.3073_2	16.090	4.279	3.634	1.612	−6.31	−0.358
0.3110_3	16.191	3.939	2.304	1.040	−5.80	−0.534
0.3465_7	16.058	4.300	3.913	2.076	−6.91	−0.292
0.4132_5	16.396	4.430	3.428	2.414	−7.78	−0.277

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

in Table 5, as well as the reported values [4,6,7] for the sake of comparison. Enthalpies of inclusion of 1,4-BD into α- and β-CD are small exothermic values. Fig. 3 shows the differences of the entropy of inclusion of the same alcohol in the cavities between β-CD and α-CD cavities. In the case of 1,4-BD the difference is nearly zero. It seems that 1,4-BD molecules have equivalently large freedom of molecular motion in both kinds of cavities.

The molar enthalpy of inclusion of 1,4-BD from ideal gas phase into α- and β-CD cavities in dilute aqueous solution at infinite dilution of 1,4-BD at 298.15 K were calculated by the method described elsewhere [7].

Table 4
Equilibrium constants for the formation of 1:1 inclusion complexes, ratios of water molecules over the cyclodextrin molecules, limiting molar enthalpies of transfer of alcohol, and the limiting molar ratios y_{max} of 1,4-BD included to the whole at 298.15 K

System	$\log_{10} K$	z	$\Delta_{\mathrm{trf}}H^{\infty}_{\mathrm{m}}$	y_{max}
α-CD+1,4-BD	4.04	4919	−1.43	0.689
β-CD+1,4-BD	3.93	6749	−0.796	0.556

Fig. 4 shows that gaseous 1,4-BD molecules are enthalpically stabilised more than 1,3-BD molecules in the cavities. The largest stabilisation in enthalpy ($\Delta_{\mathrm{inc}}H^{\mathrm{g}}_{\mathrm{m}}$: −89.5 kJ mol^{-1} in α-CD and −88.8 kJ mol^{-1} in β-CD) is obtained by the inclusion of 1,4-BD from gas phase. This stabilisation is larger than that for pentanol which is one of the isoelectronic compounds of 1,4-BD by 10.9 kJ mol^{-1}. This additional stabilisation is less than that due to a hydrogen bond formation. Therefore, those OH groups of 1,4-BD molecules may not form additional strong hydrogen bonds with oxgens of inner walls of α-CD cavities or outer water molecules. The other possibility is that the molecules of 1,4-BD are intramolecularly hydrogen bonded to make cyclic molecules in vapour phase already.

As shown in Fig. 4, 1,4-BD and 1,3-BD have respectively similar or the same values of $\Delta_{\mathrm{inc}}H^{\mathrm{g}}_{\mathrm{m}}$ in both α- and β-CD cavities, in spite of the significant differences in cavity diameters between α- and β-CD.

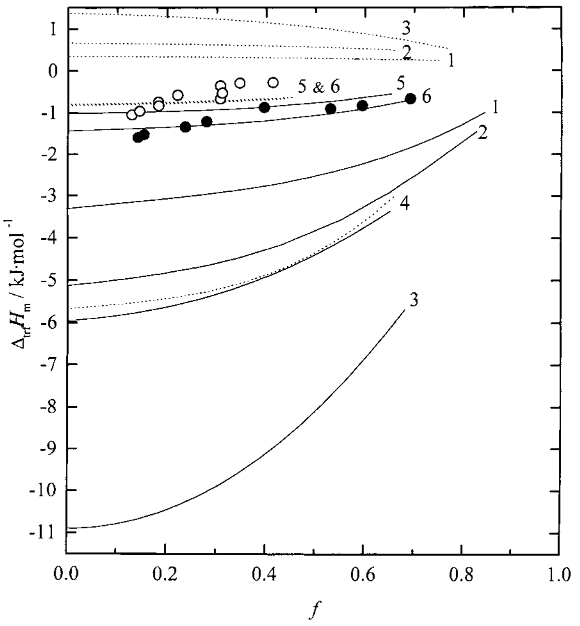

Fig. 2. Molar enthalpies of transfer at 298.15 K: (●) and (○) present results for 1,4-BD; (——) α-CD; (·········) β-CD (curves are cited from previous papers [1–7] except those for 1,4-BD): (1) 1-propanol; (2) butanol; (3) pentanol; (4) cyclohexanol; (5) 1,3-BD; (6) 1,4-BD.

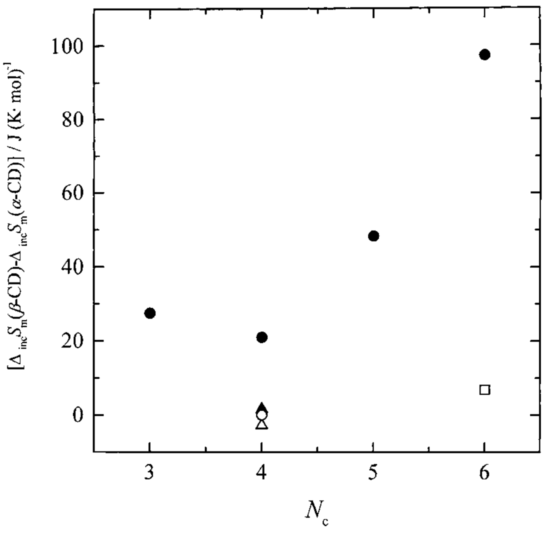

Fig. 3. Differences of entropies of inclusion of alcohols in the CD cavities between α- and β-CD's plotted against the number of carbon atoms in an alcohol molecule N_C: (●) *n*-alkane-1-ol; (▲) 1,3-BD; (○) 1,4-BD; (△) 2,3-BD; (□) cyclohexanol.

Table 5
The changes of thermodynamic functions on 1:1 inclusion of simple alcohols into α- and β-cyclodextrin cavities in dilute aqueous solutions at 298.15 K

Alcohol	$\Delta_{inc}H$ (kJ mol^{-1})	$\Delta_{inc}G$ (kJ mol^{-1})	$T\Delta_{inc}S$ (kJ mol^{-1})	$\Delta_{inc}S$ (J(K mol)$^{-1}$)
α-Cyclodexrtin				
1-Propanol [7]	−6.6	−17.8	−11.2	37.5
1-Butanol [6]	−7.9	−22.6	−14.7	49.5
1-Pentanol [7]	−13.9	−24.4	−10.4	34.9
1-Hexanol [8]	−29.1	−22.2	−6.9	−23.1
1,3-Butanediol [7]	−1.3	−24.0	−22.7	76.1
1,4-Butanediol	−2.1	−23.0	−21.0	70.3
2.3-Butanediol [9]	−1.1	−21.6	−20.5	68.8
2-Propanol [7]	−0.4	−19.2	−18.8	63.0
Cyclohexanol [7]	−7.9	−23.8	−15.9	53.3
β-Cyclodextrin				
1-Propanol [7]	1.9	−17.5	−19.4	65.0
1-Butanol [6]	3.0	−18.0	−21.0	70.5
1-Pentanol [7]	2.2	−22.6	−24.8	83.2
1-Hexanol [8]	0.6	−21.5	−22.1	74.1
1,3-Butanediol [7]	−1.4	−23.3	−21.9	73.4
1,4-Butanediol	−1.4	−22.4	−21.0	70.4
2,3-Butanediol [9]	−1.2	−22.2	−21.0	70.4
2-Propanol [7]	1.2	−19.7	−20.9	70.1
Cyclohexanol [7]	−7.0	−24.9	−17.9	60.1

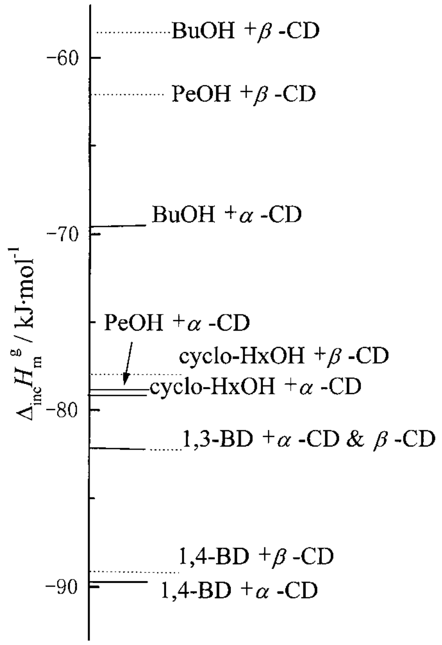

Fig. 4. Molar enthalpies of inclusion of alcohols from ideal gas phase into α(——) and β (········) -CD cavities in dilute aqueous solution at infinite dilution of the alcohols at 298.15 K. The results for other alcohols are described together for the sake of comparison [7].

These BD molecules must deform their conformations to make the closest contacts with the atoms on the wall of α-CD cavities or those on the walls of β-CD cavities and the remaining water molecules in β-CD cavities.

Bastos et al. [14] obtained (-11.7 ± 0.4) kJ mol^{-1} as the change in enthalpy for the 1:1 binding of α-CD and 1,4-BD molecules in water at 298.15 K by the careful microcalorimetric titration. However, this large value of exothermic change might be arose from smaller enthalpy of dehydration of 1,4-BD molecules before inclusion due to incomplete hydration in the initial aqueous solutions of 1,4-BD [12]. Spencer et al. [15] also reported (-8.0 ± 0.3) kJ mol^{-1}as the enthalpy change. They injected neat diol into aqueous α-CD solutions. Thus the precision and accuracy are lower than the present work. (These entries are made in reply to the comment by one of the referees.)

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