

THERMODYNAMIC FUNCTIONS OF MOLECULAR INCLUSION OF SOME ISOMERS OF BUTANEDIOL IN GAS PHASE INTO α - AND β -CYCLODEXTRIN CAVITIES IN AQUEOUS SOLUTIONS AT 298.15 K

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Abstract

The enthalpies, entropies and Gibbs energies of inclusion of *dl*-1,3-, 1,4- and *meso*-2,3-butanediols into α - and β -cyclodextrin cavities from ideal gas phase have been determined on the basis of newly obtained experimental data of the butanediols. The butanediol molecules are stabilised strongly in the cavities due to interactions with inner walls of the cavities. Entropies of the gaseous isomers are greatly decreased in the cavities. The largest decrease is obtained for the case of 2,3-BD. Discussions concerning the 1,4-butanediol given in the preceding paper have been changed due to the adoption of new data on the butanediols.

Keywords: butanediol isomers, cyclodextrin, enthalpy, entropy, Gibbs energy, inclusion from ideal gas phase, molecular recognition

Introduction

Cyclodextrin (CD) molecules include various kinds of guest molecules in their molecular cavities recognizing the difference in structures of those in aqueous solutions. To clarify the mechanism of molecular recognition and discrimination in aqueous solutions, thermodynamic functions have been determined systematically for the molecular inclusion of simple alcohols into α - and β -CD cavities in dilute aqueous solutions by the present authors [1–10].

In this paper, the molar enthalpies, entropies and Gibbs energies of inclusion of *dl*-1,3-, 1,4- and *meso*-2,3-butanediols into α - and β -CD cavities from an ideal gas phase were determined at 298.15 K, since the molar enthalpies and entropies of evaporation of the butanediol isomers were determined by the present authors by the vapour pressure measurement [11–14].

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Determination of thermodynamic functions

The experimental results of molecular inclusion in dilute aqueous solutions which were used in this paper had been obtained from the previously described experiments [7, 9, 10]. In those experiments, careful purifications were carried out for the butanediols [7, 9, 10], α -CD [1], β -CD [2], water [15] and mercury [16]. The aqueous butanediol solutions prepared were stirred for 10 min at room temperature on a magnetic stirrer. Then, they were vigorously stirred for ca 15 min at room temperature with a weak sonic washer (Taga Electric Co., Ltd., model UW-25, output frequency: 38 kHz, 45W) before charging them into mixing vessels to make sure that the mixtures are easy to reach equilibrium in holding time for measurement.

Takagi *et al.* found that the mixtures of water and 1,4-butanediol required a lot of time (max.: ca 15 h) to reach equilibria at room temperatures [17]. This information was presented before the informal meeting held at the 7th IUPAC Conference on Chemical Thermodynamics, London, 1982, and many other symposia [18–20]. These vigorous stirring by weak supersonic waves followed by standing for long time is the characteristic of our procedures different from other papers [21, 22]. Microcalorimetry used was a batch method [10, 16].

Table 1 Thermodynamic functions of inclusion at 298.15 K^a

	α -cyclodextrin			β -cyclodextrin		
	1,4-BD ^b	1,3-BD ^c	2,3-BD ^d	1,4-BD ^b	1,3-BD ^c	2,3-BD ^d
$\log_{10}K^e$	4.04	4.21	3.78	3.93	4.08	3.89
y_{\max}^f	0.689	0.761	0.538	0.556	0.600	0.565
z_{mean}^g	4919	5116	5151	6749	7936	5947
$\Delta_{\text{inc}}G/\text{kJ mol}^{-1}$	-23.0	-24.0	-21.6	-22.4	-23.3	-22.2
$\Delta_{\text{inc}}H/\text{kJ mol}^{-1}$	-2.1	-1.3	-1.1	-1.4	-1.4	-1.2
$-T\Delta_{\text{inc}}S/\text{kJ mol}^{-1}$	-21.0	-22.7	-20.5	-21.0	-21.9	-21.0
$\Delta_{\text{inc}}S/\text{J (K mol)}^{-1}$	70.3	76.1	68.8	70.4	73.4	70.4

^aAbbreviation BD means butanediol

^bFujisawa *et al.* [10]

^cTakagi *et al.* [7]

^dFujisawa *et al.* [9]

^eEquilibrium constant for the formation of 1:1 inclusion complex [3]

^fMolar ratio of butanediol included to the total one, at the infinite dilution [3]

^gMolar ratios of CD to water [3]

The thermodynamic functions reported earlier are listed in Table 1. Procedures determining the changes of thermodynamic functions when the butanediol molecules in an ideal gas state are included into the cavities of CD's in dilute aqueous solutions are illustrated in Fig. 1, as an example of the case of entropy of inclusion $\Delta_{\text{inc}}S_{\text{m}}^{\text{E.g}}$ from an ideal vapour phase. The molar enthalpies of inclusion $\Delta_{\text{inc}}H_{\text{m}}^{\text{E.g}}$ of the butanediols from ideal gas phase into the CD cavities in dilute aqueous solutions at the infi-

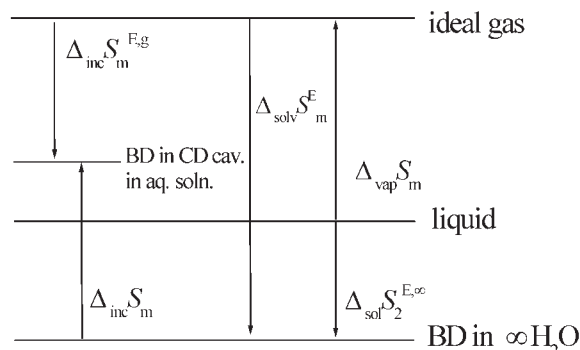


Fig. 1 Entropy diagram of butanediol (BD) showing that the entropy change on molecular inclusion of BD into the cyclodextrin (CD) cavities in aq. solution from an ideal gas phase $\Delta_{\text{inc}} S_m^{\text{E,g}}$ are obtained as the difference of the molar entropy of inclusion $\Delta_{\text{inc}} S_m$ and molar entropy of solvation $\Delta_{\text{solv}} S_m = -\Delta_{\text{vap}} S_m + \Delta_{\text{sol}} S_2^{\text{E,g}}$, where superscript E means the excess from the ideal mixtures

nite dilution of butanediols at 298.15 K were calculated by the method described earlier [7], using Eq. (1).

$$\Delta_{\text{inc}} H_m^{\text{g}} = -\Delta_{\text{vap}} H_m + \Delta_{\text{sol}} H_2^{\text{E},\infty} + \Delta_{\text{inc}} H_m \quad (1)$$

Table 2 Thermodynamic functions of inclusion of butanediols into α - and β -cyclodextrin cavities in dilute aqueous solutions from ideal gas phase at 298.15 K

Butanediol	$\Delta_{\text{inc}} H_m^{\text{g}} /$ kJ mol ⁻¹	$\Delta_{\text{inc}} S_m^{\text{E},\infty} /$ J (K mol) ⁻¹	$-T\Delta_{\text{inc}} S_m^{\text{E,g}} /$ kJ mol ⁻¹	$\Delta_{\text{inc}} G_m^{\text{E,g}} /$ kJ mol ⁻¹
α -cyclodextrin				
1,4-butanediol	-56.1	-36.4	10.9	-45.2
<i>dl</i> -1,3-butanediol	-83.0	-125.0	37.2	-45.8
<i>meso</i> -2.3-butanediol	-129.1	-281.1	83.8	-45.3
β -cyclodextrin				
1,4-butanediol	-55.4	-36.1	10.8	-44.6
<i>dl</i> -1,3-butanediol	-83.1	-127.7	38.0	-45.1
<i>meso</i> -2.3-butanediol	-129.2	-279.5	83.3	-45.9

The molar entropies and Gibbs energies of inclusion from an ideal gas phase were also determined by similar Eqs (2) and (3). The results determined are given in Table 2. In the course of calculations, values of the thermodynamic functions of evaporation of butanediols listed in Table 3 [11] were used, although the estimated values of enthalpies of evaporation reported by Ducros *et al.* [23] were used in the previous papers [7, 10].

$$\Delta_{\text{inc}} S_m^{\text{E,g}} = -\Delta_{\text{vap}} S_m + \Delta_{\text{sol}} S_2^{\text{E},\infty} + \Delta_{\text{inc}} S_m \quad (2)$$

$$\Delta_{\text{inc}} G_m^{\text{E},g} = -\Delta_{\text{vap}} G_m + \Delta_{\text{sol}} G_2^{\text{E},\infty} + \Delta_{\text{inc}} G_m \quad (3)$$

The limiting values of the partial molar excess enthalpies $\Delta_{\text{sol}} H_2^{\text{E},\infty}$, entropies $\Delta_{\text{sol}} S_2^{\text{E},\infty}$, and Gibbs energies $\Delta_{\text{sol}} G_2^{\text{E},\infty}$ of butanediols at infinite dilution are summarised in Table 4 [12–14].

Table 3 Thermodynamic functions of evaporation of butanediols at 298.15 K and 101.325 kPa^a

	$\Delta_{\text{vap}} H_m / \text{kJ mol}^{-1}$	$\Delta_{\text{vap}} S_m / \text{J (K mol)}^{-1}$	$\Delta_{\text{vap}} G_m / \text{kJ mol}^{-1}$
1,4-butanediol	43.0	65.0	23.6
<i>dl</i> -1,3-butanediol	68.8	151	23.8
<i>meso</i> -2,3-butanediol	110	283	25.6

^aTakagi and Kimura [11]

Table 4 Partial molar excess thermodynamic functions at infinite dilution for water(1)+butanediol(2) at 298.15 K

	$\Delta_{\text{sol}} H_2^{\text{E},\infty} / \text{kJ mol}^{-1}$ ^a	$\Delta_{\text{sol}} S_2^{\text{E},\infty} / \text{J (K mol)}^{-1}$ ^b	$\Delta_{\text{sol}} G_2^{\text{E},\infty} / \text{kJ mol}^{-1}$ ^b
1,4-butanediol	-10.97	-41.5	1.39
<i>dl</i> -1,3-butanediol	-12.94	-50.2	2.04
<i>meso</i> -2,3-butanediol	-18.03	-66.9	1.91

^aTakagi *et al.* [14], ^bTakagi *et al.* [12, 13]

Results and discussion

The results obtained are summarised in Table 2 and are shown in Figs 2, 3 and 4. Figure 2 shows that the CD molecules cannot discriminate a favourite isomer among the

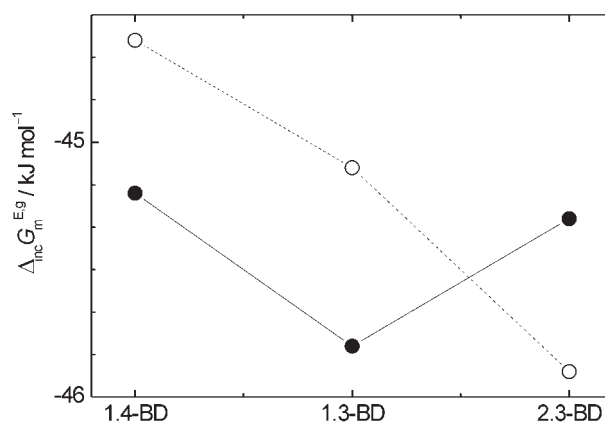


Fig. 2 Molar entropies of inclusion of butanediols into α - and β -CD cavities from an ideal gas state at 298.15 K: —●—, α -CD; —○—, β -CD

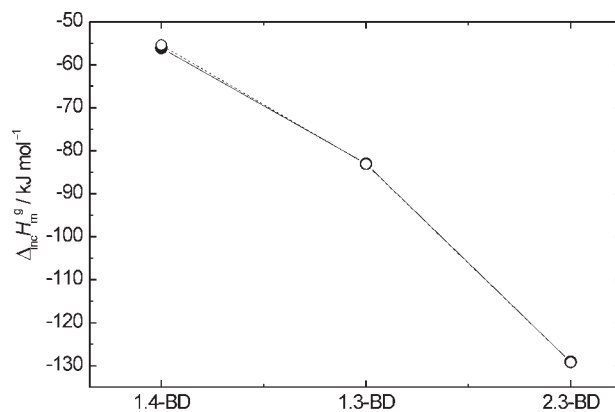


Fig. 3 Molar enthalpies of inclusion of butanediols into α - and β -CD cavities from an ideal gas state at 298.15 K: \bullet —, α -CD; \circ —, β -CD

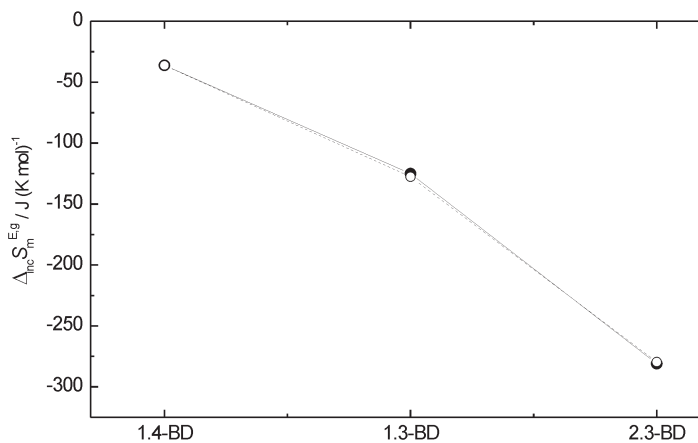


Fig. 4 Molar Gibbs energies of inclusion of butanediols into α - and β -CD cavities from an ideal gas state at 298.15 K: \bullet —, α -CD; \circ —, β -CD

three butanediol isomers and nor can the molecules of the butanediols differentiate α -CD molecules from β -CD molecules in dilute aqueous solutions. However, the butanediols largely stabilised energetically in the CD cavities as shown in Fig. 3 and Table 2. This may be well understood by comparing the values given in Table 2 with those in Table 1 and by referring to Fig. 4 in a previous paper [7].

The present results shown in Figs 3 and 4 suggest that 1,4-butanediol molecules may be included in α - and β -CD cavities in an elongated linear form, not a ring. An intramolecular hydrogen bond formed in a cyclic 1,4-butanediol molecule in a gas phase may be broken at the molecular inclusion. Molecules of 1,3- and 1,4-butanediol may form intermolecular hydrogen bonds by at least one hydroxyl group in each molecule with the oxygen atoms on the walls of the cavities for α -CD and with the

oxygen atoms on the walls or those of co-included water molecules for β -CD. For the case of 2,3-butanediol, both hydroxyl groups of 2- and 3- positions may form intermolecular hydrogen bonds with oxygen atoms on the inner walls of cavities for α -CD and with oxygen atoms of the inner walls or co-included water molecules for β -CD.

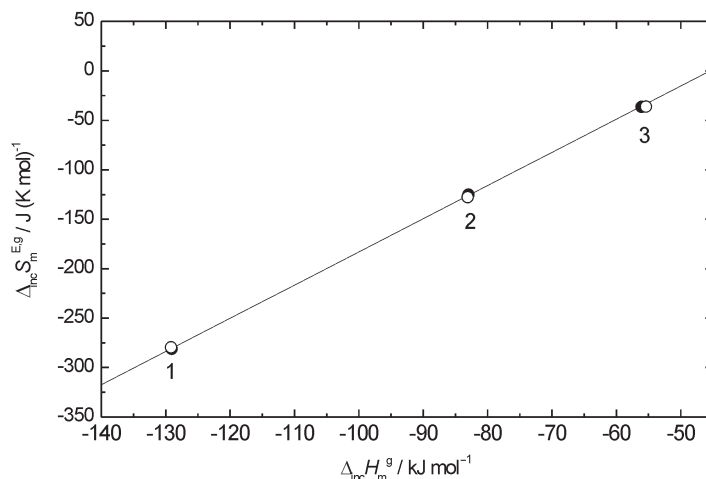


Fig. 5 Enthalpy-entropy compensation for the system of α - \bullet -CD and β - \circ -CD + BD: 1, 1,4-BD; 2, *dl*-1,3-BD; 3, *meso*-2,3-BD

The decrease in entropy of inclusion from an ideal gas phase shown in Fig. 4 corresponds to the increase in the stabilisation in enthalpy of inclusion from an ideal gas phase. The ΔH - ΔS compensation is shown in Fig. 5 for the 1:1 inclusion-complex formation between α - and β -CD with above-mentioned three isomers. Molecular rotation of 2,3-butanediol in the α -CD cavities around perpendicular axes to the molecular axis may be restricted [9].

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