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THERMODYNAMIC FUNCTIONS OF 1,2-ALKANEDIOLS IN DILUTE AQUEOUS SOLUTIONS

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Abstract

The heat capacities of binary aqueous solutions of 1,2-ethanediol, 1,2-propanediol and 1,2-butanediol were measured at temperatures ranging from 283.15 to 338.15 K by differential scanning calorimetry. The partial molar heat capacities at the infinite dilution were then calculated for the respective alkanediols. For 1,2-ethanediol or 1,2-propanediol, the partial molar heat capacities at the infinite dilution of increased with increasing temperature. In contrast, the partial molar heat capacities of 1,2-butanediol at the infinite dilution decreased with increasing temperature.

Heat capacity changes by dissolution of the alkanediols were also determined. Heat capacity changes caused by the dissolution of 1,2-ethanediol or 1,2-propanediol were increase with increasing temperature. On the other hand, heat capacity changes caused by the dissolution of 1,2-butanediol are decrease with increasing temperature. Thus our results indicated that the structural changes of water caused by the dissolution of 1,2-butanediol differed from that of the two other alkanediols.

Keywords: 1,2-alkanediol, heat capacity, hydrophobic hydration, infinite dilution

Introduction

To understand the mechanism of hydration of proteins, it is important to elucidate the effects of hydrophilic group on the hydration of hydrophobic groups. In a previous paper, we determined the enthalpies of dilution for aqueous solutions of *n*-alkane-1-ols, 1,3-butanediol, 1,4-butanediol and 2,3-butanediol at 298.15 K, using a rocking twin-microcalorimeter of the heat-conduction type. To examine interactions in dilute aqueous solutions, enthalpic interaction parameters were determined [1]. In the present paper, we investigated the temperature dependence of hydrophobic hydration by determining the experimental results for the heat capacity of binary aqueous solutions of 1,2-ethanediol, 1,2-propanediol and 1,2-butanediol.

Experimental

1,2-ethanediol (Aldrich, anhydrous grade) and 1,2-propanediol (Aldrich, anhydrous grade) were used without further purification. 1,2-butanediol (TCI) was used after drying

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with molecular sieves. Water contents by mass were obtained by Karl Fischer titration and were 0.028% for 1,2-ethanediol, 0.039% for 1,2-propanediol, and 0.080% for 1,2-butanediol. Details of the careful purification used for the water [2] were described earlier. All aqueous solutions were prepared by mass and 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 weak sonic washer (SND Co., Ltd., model ssc-7500, output frequency: 42 kHz, 70W) 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*. had 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 [3]. This information was presented before the informal meeting held at the 7th IUPAC Conference on Chemical Thermodynamics, London, 1982, and many other symposia [4–6].

Calorimetric measurements were carried out using a CSC 5100 differential scanning calorimeter (Calorimetry Science Corp. USA). Data were collected from 278 to 333 K at a heating rate of 1.0 K min^{-1}. Apparent molar volumes were calculated from densities using a precise densimeter (DMA-55, Anton Paar, Austria). Density measurements were made at 283.15, 298.15, 313.15, and 328.15 K using a water-filled thermostat controlled to 0.001 K at 283.15, 298.15 and 313.15 K, and 0.003 K at 328.15 K.

Results and discussion

The apparent molar volume of the solute in water V was calculated from the data using the following Eq. (1) [7] :

$$V=\frac{M}{d}-\frac{1000(d-d_0)}{mdd_0} \tag{1}$$

where d_0 is the density of water, d is the density of the solute and m is the molality.

The results were fitted by least-squares methods to Eq. (2) of the form

$$V=V^0+am \tag{2}$$

The molar heat capacity $\Delta C_{p,2}$ for each solute was calculated from the data using the following Eq. (3), with the values of limiting apparent molar volume for each alkanediols at various temperatures calculated using Eq. (3) are listed in Table 1.

Table 1 Limiting apparent molar volumes of alkanediols at various temperatures

Compounds	T/K 283.15	298.15	313.15	328.15
	V^0/cm^3 mol^{-1}			
1,2-ED	54.0	55.6	56.2	57.6
1,2-PD	69.8	71.4	72.8	73.7
1,2-BD	85.9	86.4	87.8	88.1

$$C_{\mathrm{p},2}=\frac{M\Delta C_{\mathrm{p}}}{w}+\frac{C_{\mathrm{solv}}}{V_{\mathrm{solv}}}V^{0} \tag{3}$$

where M is the molecular mass of the solute, ΔC_{p} is the apparent molar heat capacity of the solute, w is mass of the solute, C_{solv} is the molar heat capacity of water, V_{solv} is the molar volume of water and V_0 is the partial molar volumes of the alkanediols at the infinite dilution.

The results were fitted by least-squares methods to Eq. (4) of the form

$$C_{\mathrm{p},2}=C^{\infty}_{\mathrm{p},2}+am \tag{4}$$

where $C^{\infty}_{\mathrm{p},2}$ is the partial molar heat capacity at infinite dilution.

Heat capacity changes by dissolution of alkanediols are determined by Eq. (5):

$$\Delta C^{\infty}_{\mathrm{p},2}=C^{\infty}_{\mathrm{p},2}-C_{\mathrm{p},1} \tag{5}$$

where $C_{\mathrm{p},1}$ is heat capacity of each alkanediol in the liquid state.

The hydration heat capacity was determined by Eq. (6):

$$\Delta C^{\mathrm{hydro}}_{\mathrm{p},2}=C^{\infty}_{\mathrm{p},2}-C^{*}_{\mathrm{p,g}} \tag{6}$$

where $C^{*}_{\mathrm{p,\,g}}$ is the heat capacity of each alkanediol in the gaseous state.

The values of $C^{\infty}_{\mathrm{p},2}$ and $\Delta C^{\mathrm{hydr}}_{\mathrm{p},2}$ at various temperatures are listed in Table 2 and are shown in Figs 1 and 2. The values of $C^{\infty}_{\mathrm{p},2}$ and $\Delta C^{\mathrm{hydr}}_{\mathrm{p},2}$ at various temperatures were all positive, and the followed the order 1,2-ethanediol < 1,2-propanediol < 1,2-butanediol. This suggested the water molecules around a 1,2-butanediol form strongly hydrogen bonds.

Results shown in Fig 2 suggested that 1,2-butanediol exhibited a higher hydrophobicity compared to the other alkanediols. As 1,2-ethanediol lacks an alkyl group, its hydrophobicity is the lowest among the 1,2-alkanediols. The water accessible surface area (ASA) for alkanediols was calculated by computer modeling [7], with the water accessible surface area of hydrophobic groups (ASA(hydpho)) for each alkanediol determined by Eq. (7)

ASA(hydpho)=ASA[100–ASA(hydphi)%]/100 =ASA[ASA(hydpho)%]/100 (7)

where ASA(hydphi)% is the proportion of the water accessible surface areas of hydrophilic groups [8]. For instance, the value of 1,2-butanediol was determined as follows.

1,2-Butanediol[ASA(hydpho)]=2.705(100.0–58.35)/100=1.127

Water accessible surface areas values for hydrophobic groups are listed in Table 3, along with values calculated for α,ω-alkanediols for comparison. The proportions of hydrophobic group water accessible surface areas for 1,2-alkanediols were higher than those for α,ω-alkanediols. Likewise, 1,2-alkanediol showed larger water accessible surface areas of hydrophobic groups than α,ω-alkanediols. The values of

Table 2 Partial molar heat capacities of 1,2-alkanediol at the infinite dilution $C^{\infty}_{p\,2}$ showing increments $\Delta C^{\infty}_{p\,2}=C^{\infty}_{p\,2}-C^{*}_{p\,2}$ and increments $\Delta C^{\mathrm{hydr}}_{p\,2}=C^{\infty}_{p\,2}-C^{*}_{p\,g}$ at various temperatures

T/K	$C^{\infty}_{p\,2}$/ J K^{-1} mol^{-1}	$C^{*}_{p\,1}$/ J K^{-1} mol^{-1}	$C^{*}_{p\,g}$/ J K^{-1} mol^{-1}	$\Delta C^{\infty}_{p\,2}$/ J K^{-1} mol^{-1}	$\Delta C^{\mathrm{hydr}}_{p\,2}$/ J K^{-1} mol^{-1}
		1,2-Ethanediol			
283.15	189.3	163.8[a]	96.6[a]	25.5	92.7
298.15	197.9	165.5[a]	98.8[a]	32.4	99.1
313.15	214.0	167.1[a]	101.0[a]	46.9	113.0
328.15	216.6	168.7[a]	103.2[a]	47.9	113.4
		1,2-Propanediol			
283.15	289.1	210.2[a]	102.3[a]	78.9	186.8
298.15	294.0	213.3[a]	107.1[a]	81.7	186.9
313.15	298.8	214.5[a]	112.0[a]	84.3	186.8
328.15	304.9	216.8[a]	117.1[a]	88.1	187.8
		1,2-Butanediol			
283.15	404.4	221.4[b]	121.7[c]	183.0	282.7
298.15	398.4	231.6[b]	126.0[c]	166.8	272.4
313.15	394.4	241.1[b]	130.2[c]	153.4	264.2
328.15	385.7	250.0[b]	134.5[c]	135.7	251.2

[a]Yaws *et al.* [11]; [b]Yeh [12]; [c]Poling *et al.* [13]

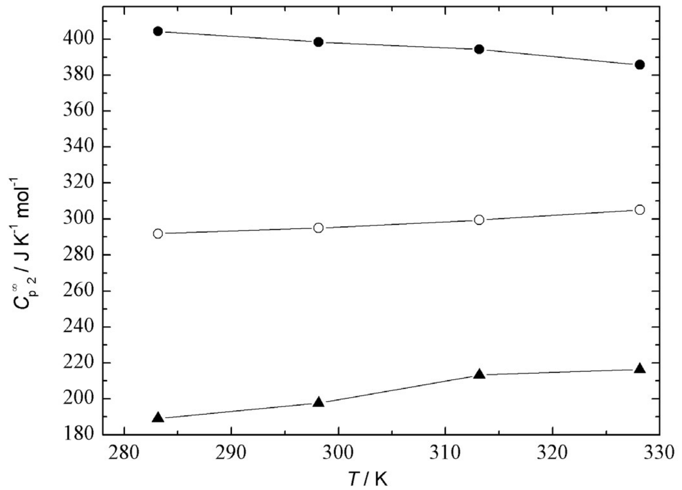

Fig. 1 Temperature dependence of the partial molar heat capacity for each alkanediols at infinite dilution: ▲ – 1,2-ethanediol; ○ – 1,2-propanediol; ● – 1,2-butanediol

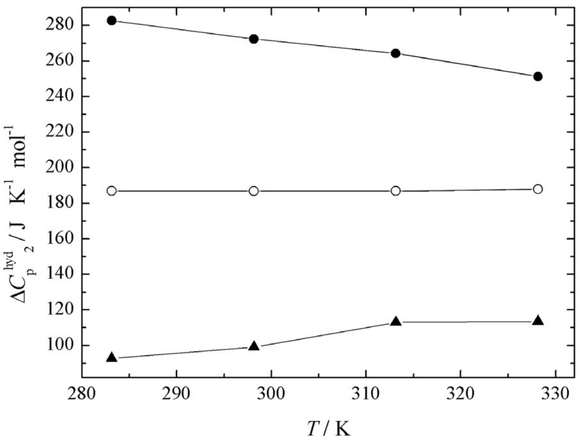

Fig. 2 Temperature dependence of heat capacity increments of hydration for alkanediols: ▲ – 1,2-ethanediol; ○ – 1,2-propanediol; ● – 1,2-butanediol

$\Delta C_{p,2}^{hydr}$ calculated for 1,2-alkenediols and α,ω-alkanediols were plotted *vs.* water accessible surface areas of hydrophobic groups for alkanediols (Fig. 3). The values of $\Delta C_{p,2}^{hydr}$ (J K^{-1} mol^{-1}) for α,ω-alkanediols [9] were: 1,3-propanediol=168.0, 1,4-butanediol=222.8, 1,5-pentanediol=292.0, 1,6-hexanediol=351.6. Values for 1,2-alkanediols (solid line) and α,ω-alkanediols (dotted line) were calculated by the least-squares method. 1,2-alkanediols showed larger hydration quantities per ASA (hydpho) than α,ω-alkanediols.

Values of $\Delta C_{p,2}^{\infty}$ at various temperatures are listed in Table 2 and are shown in Fig. 4. When 1,2-alkanediols transfer from their pure liquid into water, the $\Delta C_{p,2}^{\infty}$ values were much greater than zero. This suggested that 1,2-alkanediols surrounded by water showed greater affinities than in their corresponding pure liquid states. The $\Delta C_{p,2}^{\infty}$ values were mainly due to the structural changes of water caused by the dissolution of the alkanediols. As the thermal motion of water molecules in the hydration shell around a 1,2-ethanediol is less inhibited than that of around the other two alkanediols, the $\Delta C_{p,2}^{\infty}$ value for 1,2-ethanediol is smallest among the 1,2-alkanediols. While the heat capacity

Table 3 Molecular surface areas of alkanediols

Compounds	ASA/nm^2	ASA(hydropho)/%	ASA(hydro)/nm^2
1,2-Ethanediol	2.224	0.00	0.000
1,2-Propanediol	2.443	30.41	0.7428
1,2-Butanediol	2.705	41.65	1.127
1,3-Propanediol	2.608	46.14	1.203
1,4-Butanediol	2.886	52.24	1.508
1,5-Pentanediol	3.245	61.13	1.984
1,6-Hexanediol	3.640	65.89	2.398

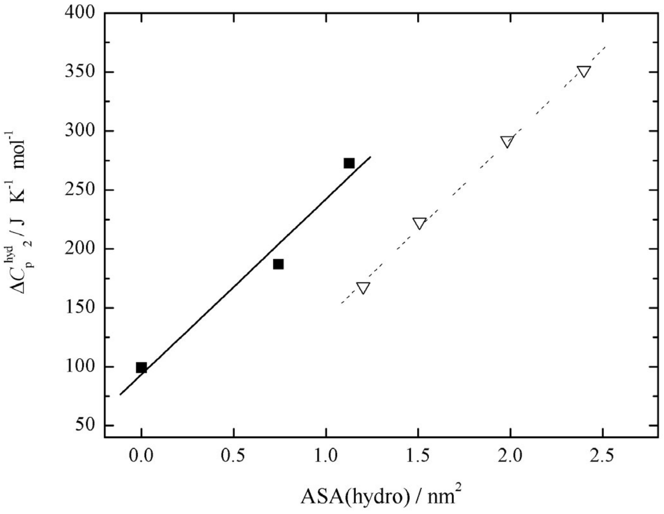

Fig. 3 Heat capacity of hydration for alkanediols at infinite dilution at 298.15 K *vs.* the water accessible surface areas of the alkanediols hydrophobic groups: ■ – 1,2-alkanediol; ▽ – α,ω-alkanediol

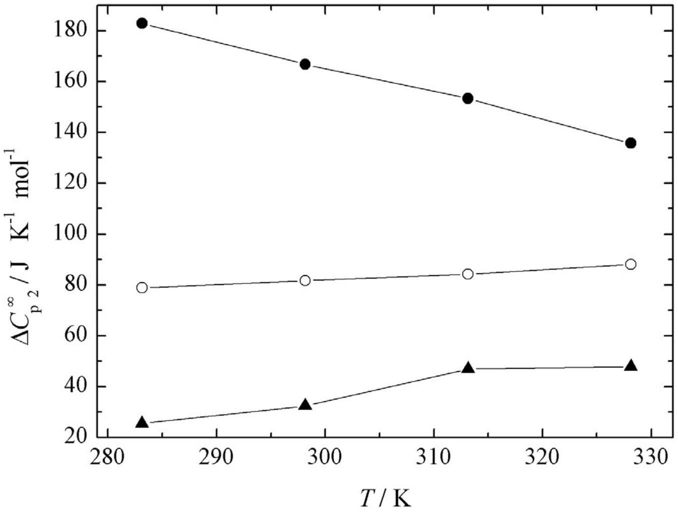

Fig. 4 Temperature dependence of heat capacity increments of dissolution for each alkanediols: ▲ – 1,2-ethanediol; ○ – 1,2-propanediol; ● – 1,2-butanediol

changes during dissolution of 1,2-ethanediol and 1,2-propanediol increased with increasing temperature, heat capacity changes during dissolution of 1,2-butanediol decreased with increasing temperature. Thus, it appeared that the structural changes of water caused by the dissolution of 1,2-butanediol differ from that of the other two alkanediols. As 1,2-butanediol have methyl groups in contact with the OH groups of the molecule, the behavior of 1,2-butanediol in aqueous solutions can be assumed to be similar to that of *n*-alkane-1-ols [10].

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