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EXCESS ENTHALPIES OF WATER+1,4-DIOXANE AT 278.15, 298.15, 318.15 AND 338.15 K

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The excess molar enthalpies of (1–x)water+x1,4-dioxane have been measured at four different temperatures. All the mixtures showed negative enthalpies in the range of low mole fraction but positive ones in the range of high mole fraction of 1,4-dioxane. Excess enthalpies were increased with increasing temperature except those of at 278.15 K. Partial molar enthalpies have maximum around x=0.13 and minimum around x=0.75. Three different behaviors for the concentration dependence of partial molar enthalpies were observed for all temperature. Theoretical calculations of molecular interactions of three characteristic concentrations were carried out using the molecular orbital method.

Keywords: *excess enthalpy, partial molar enthalpy, theoretical calculation, water+1,4-dioxane*

Introduction

The behaviors of aqueous solution of aliphatic alcohols showed one of the most attractive results [1], when size of hydrophobic part of alcohol was changed. The interesting behavior of excess enthalpies of water+ethanol from 298.15 to 323.15 K were reported by Larkin [2] to understand the hydrogen-bonding behaviors between water and ethanol. The excess enthalpies curve at 331.15 K has two minimums of enthalpy, is unusual in showing exothermal mixing for mixtures of water rich area, endothermic mixing in the middle of the composition range, and exothermal mixing again for mixtures of ethanol rich composition. The curves at 343.15 and 363.15 K are sigmoid in shape with exothermal and endothermic parts but at 383.15 K mixing is endothermic at all compositions. It is expected that the mixing curve at low temperature shows very interesting behavior by means of hydrogen-bonding and hydrophobic interactions. Consequently, the measurement of water+1,4-dioxane system was carried out. 1,4-Dioxane is amphiphilic solvent which has a ring in the structure. It consists of two polar parts of ether group and four non polar parts of ethylene group. So some interactions between water and 1,4-dioxane might be complexly affected by each other. From the interesting expectation, the excess enthalpies of water+1,4-dioxane at 298.15 and 318.15 K were reported by Goates *et al*. [3], Belousov *et al*. [4] and Morcom *et al*. [5] and showed exothermic and endothermic behavior in different compositions. However, in order to know the hydrogen-bonding and hydrophobic behaviors in water for such as a ring structure compound which have hydrophobic parts and hydrophilic parts, the temperature dependence of the excess enthalpy of water+1,4-dioxane are investigated. In this paper, excess enthalpies at 278.15, 298.15, 318.15 and 338.15 K have been measured over a whole composition range to understand behavior of water and amphiphilic ring compound of 1,4-dioxane.

Experimental

Material and methods

1,4-Dioxane (Spectra grade, Kishida Kagaku Co. Ltd.) was fractionally distilled over freshly activated molecular sieves 4A which had been evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa. G.l.c. results obtained by using each 2-m column of 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with FID on Yanagimoto G180FP showed merely some trace-impurity peaks ($<10^{-7}$). Coulometric Karl–Fischer's method on a Moisturemeter (Mitsubishi Chemical Ind., CA-02) gave the water content of each sample to be 0.01 mol% or less. Water was purified as same as previous method [6].

The structure of 1,4-dioxane was obtained from chemfinder [7]. The molecular geometry of 1,4-dioxane was minimized with the MMFF94s force field by using the COMFLEX5 program [8]. The lowest energy structure of conformation search was performed by COMFLEX5 program with the MMFF94s force

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field. This program has the following feature; the lowest energy conformer does not depend on the initial structure that user input. The obtained lowest energy conformer was the initial structure of the ab initio molecular orbital calculations. Geometry optimization by ab initio molecular orbital calculations was performed by using Gaussian 03 program [9].

The conduction microcalorimeter [10–12] (Setaram Model BT2.15, Lyon France) was kept in thermostatted room. Excess enthalpies of mixing were measured at the 278.15±0.001, 298.15±0.001, 318.15±0.001 and 338.15±0.001 K. The temperature of the calorimeter calibrated by using precision platinum resistance thermometer (AΣΛ F25).

Samples mass of water and 1,4-dioxane were precisely measured by semi-microbalance (Mettler AT261) and loaded separately into each separated room of a measurement vessel. Sample vessels were loaded into the calorimeter and kept until the sample temperature reached to the thermostatted temperature of the calorimeter. Then a separator in a vessel was removed and the samples were mixed.

Calibration in energy was performed by a defined amount of energy, electrically generated by Joule-effect device (Setaram, EJ2), within the sample cell. Each current to Joule's modules were measured by Digital Multimeter (Keythelley 196) with four wires method.

Results and discussion

Excess enthalpies of mixing of water+1,4-dioxane at 278.15, 298.15, 318.15 and 338.15 K were listed in Table 1. The enthalpies of mixing of (1–*x*)water+*x*1,4-dioxane at 298.15 K were plotted in Fig. 1a with the results of Goates *et al.* [3], Belousov *et al.* [4] and Morcom *et al.* [5]. As shown in Fig. 1a, minimum and maximum values of excess enthalpies of Goates *et al.* [3] were about 5 and 17% smaller than those of this work, respectively. The enthalpies of mixing at 318.15 K were plotted with the results of Morcom *et al.* [5] in Fig. 1b. The minimum and maximum values of excess enthalpies of Belousov *et al.* [4] were about 7% larger and 19% smaller than those of this work, respectively. The excess enthalpies of Morcom *et al.* [5] showed comparatively good agreement with this work at 298.15 and 318.15 K as shown in Figs 1a and b within about 5 and 6%, respectively.

Excess enthalpies of mixing at 278.15, 298.15, 318.15 and 338.15 K were plotted in Fig. 2, and fitted with Redlich–Kister type Eq. (1) by means of least square method, and coefficients of Eq. (1) were listed in Table 2 with the standard deviations of fits s_f (2). Smoothing values of Eq. (1) with coefficients in Table 2 were also shown in Fig. 2.

$$H^E\ [\mathrm{J\ mol^{-1}}]=(1-x)x\sum_{i=1}^{k}A_i\,(1-2x)^{i-1} \tag{1}$$

$$s_f=\sqrt{\frac{\sum_{i=1}^{n}[H^E_{obs}-H^E_{calc}]^2}{n-k}} \tag{2}$$

The enthalpies of mixing of (1–*x*)water+*x*1,4-dioxane at 278.15 K could measure in the range from *x*=0 to 0.7, because the mixtures of super cooled liquid of 1,4-dioxane were not stable, those were crystallized in the calorimeter over *x*=0.7 [13]. Exothermic behaviors in the range of water rich region were shown for four temperatures observed. It is shown that the new strong hydrogen bonds might be formed in the range of water rich region, and these systems were stable state than before the mixing. However, the excess enthalpies were shown endothermic behavior in the range of water poor region over *x*=0.4. Excess enthalpies of mixing at 298.15, 318.15 and 338.15 K showed the similar behaviors over the whole range of concentration.

Enthalpic stabilization on mixing of water+1,4-dioxane decreased with increasing tempera-

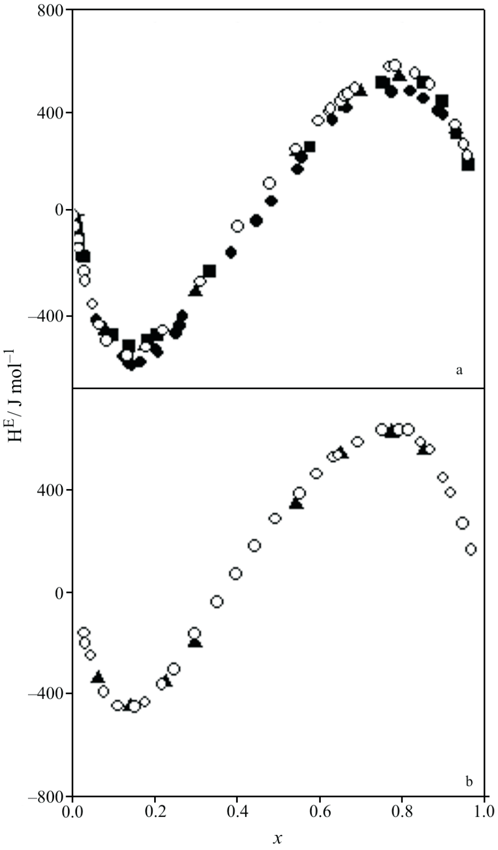

Fig. 1 Excess enthalpies of (1–*x*)water+*x*1,4-dioxane: a – 298.15 and b – 318.15 K; ● – Goates *et al.* [3], ■ – Belousov *et al.* [4], ▲ – Morcom *et al.* [5] and ○ – this work

Table 1 Excess enthalpies of (1–x)water+x1,4-dioxane

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
278.15 K					
0.004830	–44.73	0.12483	–531.8	0.33349	–229.4
0.01092	–96.06	0.12758	–534.6	0.39106	–113.1
0.03313	–255.9	0.13418	–534.4	0.40475	–92.85
0.03992	–299.2	0.15033	–523.0	0.42869	–41.82
0.04244	–307.7	0.17004	–508.3	0.43809	–13.52
0.04879	–340.7	0.19691	–482.9	0.47749	64.57
0.04956	–438.8	0.22235	–436.6	0.48853	89.91
0.05000	–354.2	0.23630	–419.3	0.51469	146.9
0.05148	–360.0	0.26506	–362.6	0.53969	195.0
0.06575	–417.6	0.27989	–338.0	0.55121	213.2
0.07916	–468.0	0.29398	–301.7	0.56940	233.7
0.09211	–498.1	0.29726	–296.5	0.59075	268.3
0.10837	–527.4	0.30096	–291.0	0.62894	288.0
0.10971	–520.2				
298.15 K					
0.0008800	–9.120	0.21895	–456.8	0.65937	465.1
0.00543	–53.60	0.30865	264.2	0.67064	471.5
0.01093	–104.2	0.39920	–52.54	0.68685	490.5
0.01465	–135.4	0.47668	117.6	0.76755	575.1
0.02594	–225.9	0.47961	118.7	0.78396	578.6
0.03071	–261.5	0.54208	254.4	0.83241	551.2
0.04753	–355.7	0.59731	361.8	0.86937	504.6
0.06306	–434.3	0.62234	399.3	0.92833	350.4
0.08140	–491.9	0.62697	408.5	0.95079	274.5
0.13076	–556.7	0.65285	442.8	0.95881	229.3
0.17720	–525.5				
318.15 K					
0.02481	–162.5	0.34894	–39.95	0.75128	630.6
0.03076	–200.3	0.39520	73.31	0.79505	633.7
0.03975	–244.8	0.44199	180.3	0.81496	631.8
0.07641	–389.1	0.49127	283.0	0.84628	585.5
0.11008	–444.7	0.55065	382.8	0.86718	554.6
0.14767	–452.5	0.59296	459.0	0.90253	449.0
0.17499	–431.5	0.63444	526.6	0.92014	389.5
0.21637	–361.6	0.64526	533.0	0.94919	263.3
0.24645	–303.3	0.69232	587.0	0.96976	162.0
0.29733	–164.4				
338.15 K					
0.01956	–98.11	0.34209	85.19	0.74501	740.8
0.04963	–210.7	0.39861	233.3	0.76701	730.3
0.06956	–250.6	0.44215	349.6	0.79557	699.8
0.07056	–254.1	0.44394	352.1	0.80237	688.6
0.07806	–266.4	0.47235	415.0	0.82907	649.4
0.09399	–295.6	0.48857	446.5	0.85512	599.8
0.11899	–319.6	0.51919	511.8	0.86638	579.5
0.13852	–320.7	0.54389	567.1	0.88303	534.4
0.14792	–310.4	0.55243	590.0	0.91085	438.5
0.15272	–308.4	0.59428	652.7	0.92027	404.0
0.19763	–252.9	0.66130	719.6	0.95236	261.1
0.24756	–155.5	0.69499	743.3	0.98167	111.6
0.29609	–36.37	0.73393	740.5		

ture except for the results at 278.15 K. It might be decrease of number of hydrogen bonds in the mixtures by increasing temperature.

The maximum and minimum at four temperatures are listed in Table 3. The minimum and maximum values of excess enthalpies observed temperatures appeared at around x=0.13 and 0.78, respectively. The minimum of exothermic enthalpies and maximum of endothermic enthalpies observed temperatures were decreased and increased with increasing temperature respectively, except at 278.15 K.

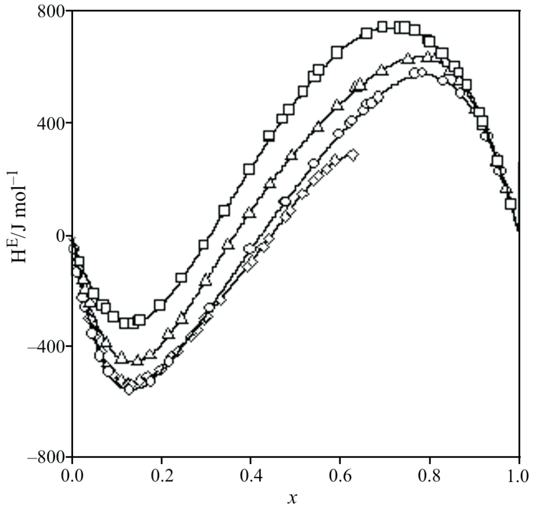

Fig. 2 Excess enthalpies of (1–x)water+x1,4-dioxane: ◇ – 278.15, ○ – 298.15, △ – 318.15 and □ – 338.15 K. The lines showed the soothing values of Eq. (1) with coefficients of Table 2

The partial molar enthalpies of H_1^E of water and H_2^E of 1,4-dioxane calculated from Eq. (1), and was shown in Fig. 3. Partial molar enthalpies of water and 1,4-dioxane may be categorized by three parts. Part I was the region of $x<0.3$, and which changed large negative to positive partial molar enthalpies for 1,4-dioxane. Part II is $0.3<x<0.8$, which showed almost constant partial molar enthalpies. Part III was the range of $x>0.8$. At the lower concentration of Part I, H_2^E increased rapidly increased with concentration of 1,4-dioxane until $x=0.2$ and all H_2^E showed maximum value around $x=0.3$. Enthalpic stabilization of H_2^E were decreased with increasing temperature except for the results at 278.15 K as shown in Fig. 4. Partial molar enthalpies of water were negative and almost constant at Part II from $x=0.3$ to 0.5. Enthalpic stabilization of partial molar enthalpies of 1,4-dioxane were decreased with increasing temperature. And those concentration span which showed almost constant partial molar enthalpies, become narrower with increasing temperature. Partial molar enthalpies of 1,4-dioxane and water showed positive values at Part III. The number and strength of hydrogen-bonding between water and 1,4-dioxane might be affected on enthalpic behavior very strongly. However, H_1^E decreased rapidly with decreasing the concentration between $x=1$ and 0.7. That means water molecules in the aqueous solution of 1,4-dioxane over $x=0.7$ were unstabilized on mixing.

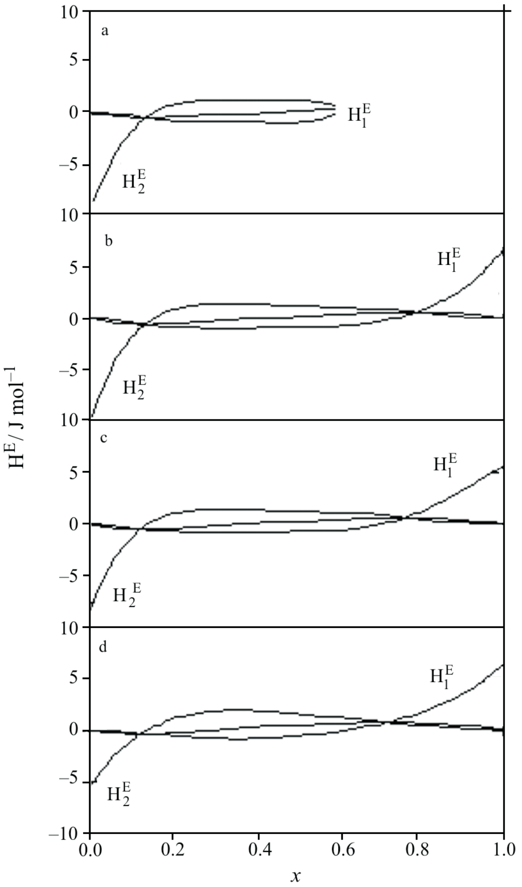

Fig. 3 Excess partial molar enthalpies of (1–x)water+x1,4-dioxane: a – 278.15, b – 298.15, c – 318.15 and d – 338.15 K

Part I might be shown that hydrogen bonding network of water might be increased by so-called hydrophobic hydration. Partial molar enthalpies of 1,4-dioxane were a little positive but those of water were large positive in Part III. The hydrogen-bonding in pure water might be broken but a little hydrogen-bonding between water and 1,4-dioxane might be formed or quadrupole interaction between 1,4-dioxane become better conformation. When partial molar enthalpies of binary mixture were constant, those intermolecular interactions must be constant whenever total molar ratio of each component was changed. The solution in this concentration region might consist of a cluster of water rich cluster and a

Table 2 Best fits coefficients A_i of Eq. (1) and the standard deviations of the fit s_f

Temperature/K	A_1	A_2	A_3	A_4	A_5	A_6	s_f/J mol^{-1}
278.15	445.0	–4169.2	–941.8	–6877.5	–22777	11170	3.7
298.15	672.2	–4151.0	–504.3	–3659.8	–2013.5	–619.9	4.3
318.15	1145.3	–4028.1	1138.3	–3084.7	–2707.0	30.8	3.4
338.15	1921.3	–4347.0	–1445.6	–1630.8	–58.6		3.3

Table 3 Minimum and maximum values of excess enthalpy of (1–x)water+x1,4-dioxane

T/K	Minimum		Maximum	
	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
278.15	0.11367	–524.2		
298.18	0.13720	–554.7	0.78061	569.4
318.15	0.12474	–433.5	0.76292	641.1
338.15	0.12831	–312.8	0.71923	744.1

Table 4 Partial molar excess enthalpies at infinite dilution of (1–x)water+x1,4-dioxane

T/K	$H_1^{E,\infty}$/kJ mol^{-1}	$H_2^{E,\infty}$/kJ mol^{-1}
278.15		–9.39
298.18	6.58	–10.3
318.15	5.66	–8.56
338.15	6.39	–5.56

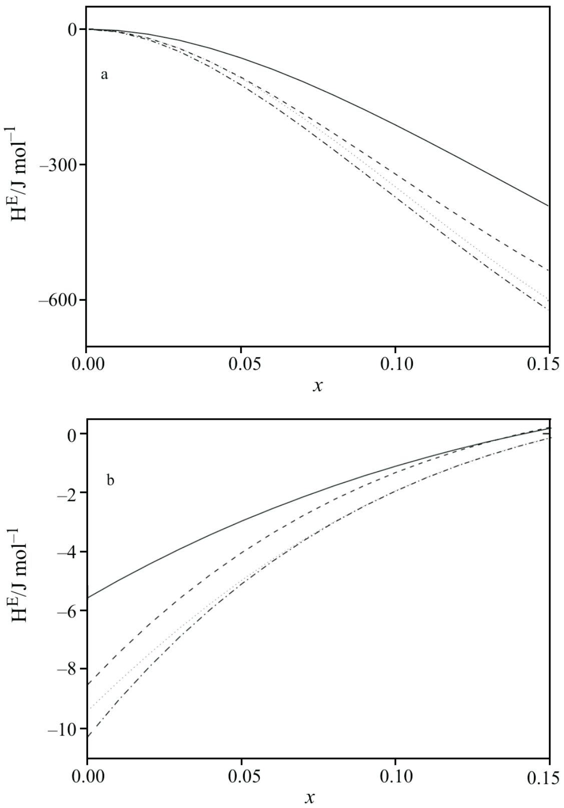

Fig. 4 Temperature dependence of partial molar enthalpies on (1–x)water+x1,4-dioxane in dilute concentration: a – partial molar enthalpies of water and b – partial molar enthalpies of 1,4-dioxane; at ··· – 278.15, –·–·– – 298.15, – – – – 318.15 and —— – 338.15 K

cluster of 1,4-dioxane rich cluster. When the total mole fraction was changed in Part II, the size of clusters were only changed to keep constant partial molar enthalpies that is excess enthalpies might consist of formation of those two kinds of clusters in Part II. And these clusters might be decreased with increasing temperature. These behaviors were very similar to the mixture of water+ethanol reported by Larkin [2]. They denominated a pseudo-two-phase system. The mixtures consisted microscopic clusters of stabilized water in dynamic equilibrium with a random mixture of water+1,4-dioxane. The molecule of 1,4-dioxane and ethanol have two surfaces of hydrophobic and hydrophilic part. Molecular interaction behaviors between those two parts of amphiphilic molecules and water might be competitive in the solutions. In order to know the molecular configuration of water and 1,4-dioxane for above three parts, the lowest energy conformers were determined by the ab initio molecular orbital calculations. Geometry optimization by ab initio molecular orbital calculations were carried out, at the RHF/6-31G(d) level and the RHF/STO-3G level theory [13]. Molecular ratios of water/1,4-dioxane calculated were 18/3, 8/13 and 4/17 which corresponded to mole fraction of x=0.14, 0.59 and 0.81, respectively. The lowest energy conformers of three concentrations were shown as Fig. 5. As shown in Fig. 5, there were no hydrogen-bonding between water and 1,4-dioxane. Here hydrogen-bonding showed by dotted lines. The network structures in those concentrations of water were increased as hydrophobic hydration in Part I shown in Fig. 5a. In Part II as shown in Fig. 5b, the network structure of water was not stronger as Part I, but water and 1,4-dioxane might be constructed different clusters each other. In Part III as shown in Fig. 5c, waters were less hydrogen-bonding compared with Parts I and II. And water

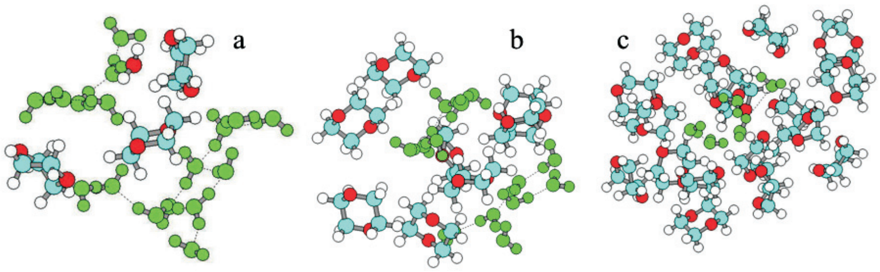

Fig. 5 Lowest energy conformation of aqueous solutions of 1,4-dioxane by means of ab initio molecular orbital calculations: a – x=0.14, b –x=0.59 and c – x=0.81

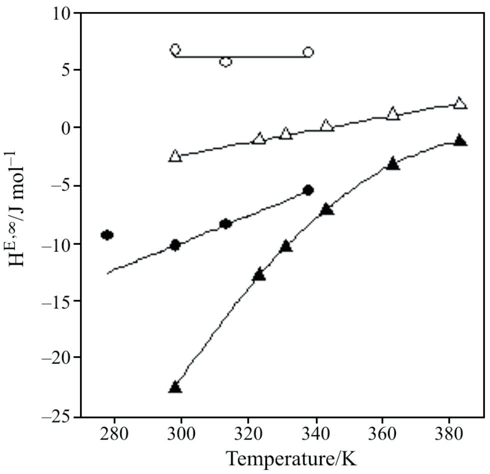

Fig. 6 Temperature dependences of partial molar enthalpies at infinite dilution: systems of ○,● – water+1,4-dioxane, ▲,△ – water+ethanol; partial molar enthalpies of ○,△ – water, ●,▲ – 1,4-dioxane or ethanol

molecules seem to be in the cage of 1,4-dioxane with less hydrogen-bonding water. These configurational figures from the ab initio molecular orbital calculations were consistent of scheme from concentration dependence of partial molar enthalpies.

The partial molar enthalpies at the infinite dilution $H_i^{E,\infty}$ were calculated by Eq. (1) with coefficients in Table 2 and listed in Table 4. Temperature dependences on the partial molar enthalpies at an infinite dilution were shown in Fig. 6 with those of water+ethanol mixtures [2]. Temperature dependences of those partial molar excess enthalpies were similar for both systems. $H_1^{E,\infty}$ at all temperatures were more positive than $H_2^{E,\infty}$, that is less enthalpically stable. Partial molar enthalpies at infinite dilution of water+1,4-dioxane were less stable than those of water+ethanol. Partial molar enthalpies of water+1,4-dioxane and water+ethanol were increased with increasing temperature. $H_2^{E,\infty}$ of water+1,4-dioxane were shown linearly increasing but those of water+ethanol were non-linearly as shown in Fig. 6.

Temperature dependence of $H_2^{E,\infty}$ of water +1,4-dioxane were fitted by Eq. (3):

$$H_2^{E,\infty}\ [\mathrm{kJ\ mol^{-1}}]=-45.9+0.1186T\ s_f=0.51\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

The extrapolated value of $H_2^{E,\infty}$ at 278.15 K from Eq. (3) was –12.9 kJ mol^{-1} and the value was 3.5 kJ mol^{-1} less stable than observed value at 278.15 K as shown in Table 4. Melting point of 1,4-dioxane is 284.95 K. So liquid state of 1,4-dioxane is metastable at 278.15 K. Heat capacity of 1,4-dioxane is 150.7 J K^{-1} mol^{-1} at 298.15 K. If the heat capacity of 1,4-dioxane can extrapolate to 278.15 K, enthalpy difference of 1,4-dioxane between 278.15 and 284.95 K is 1.02 kJ mol^{-1}. It might be change of hydrogen-bonding scheme of water at 277.13 K. On the other hand, the partial molar excess enthalpies $H_1^{E,\infty}$ of water at infinite dilution in 1,4-dioxane were almost constant of 6.21±0.49 kJ mol^{-1}, and positive values, even the partial molar excess enthalpies of 1,4-dioxan were shown large temperature dependence with negative values. As shown in Fig. 6, those of water+ethanol system showed large temperature dependence than those of water+1,4-dioxane. $H_1^{E,\infty}$ of aqueous solution of 1,4-dioxane were positive but those of aqueous solution of ethanol were negative. That was major difference between aqueous solution of 1,4-dioxane and ethanol. Water molecules in the high concentration of aqueous solution of 1,4-dioxane might be inhibited the interaction between 1,4-dioxane also be decreased the number of hydrogen-bonding with water. The scheme did not inconsistent with theoretical calculation.

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