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THERMODYNAMIC PROPERTIES OF THE MIXTURE [x 1,3-DIOXANE+(1–x) 1,4-DIOXANE] AT THE TEMPERATURE 298.15 K

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Abstract

Excess enthalpies, excess heat capacities, excess volumes and sound velocities of the mixture of dioxane isomers, 1,3-dioxane and 1,4-dioxane, were measured. One of the isomers, 1,4-dioxane is considered as non-polar liquid and the other as polar liquid. Excess enthalpies are positive and small, less than 55 J mol^{-1}. Excess heat capacities are also very small and the curve is W-shaped, and the values are from 0.03 to –0.08 J mol^{-1} K^{-1}. Excess volumes and excess isentropic compressibilities are small and positive, and less than 0.03 cm^3 mol^{-1} and 0.8 TPa^{-1}.

Keywords: excess enthalpy, excess heat capacity, excess isentropic compressibility, excess volume, mixture of dioxane isomers

Introduction

Excess thermodynamic properties of some mixtures containing dioxane isomers have been reported [1–5]. It has been revealed therein that 1,4-dioxane generally considered as a non-polar solvent in fact behaves in a similar way to 1,3-dioxane, as polar one, and that the bond dipole of 1,4-dioxane plays an important role in the mixtures. In this paper, the mixture [x1,3-dioxane+(1–x) 1,4-dioxane] is taken, and the excess enthalpies, excess heat capacities, densities and sound velocities are measured at 298.15 K. Excess volumes and excess isentropic compressibilities were estimated by using densities and sound velocities. The results are discussed in relation to polarities of isomers.

Experimental

Both of dioxane isomers, 1,3-dioxane and 1,4-dioxane (Wako Pure Chemical, chemical pure grade and special reagent grade, respectively) were fractionally distilled on metal sodium by column packed with helipac. No impurity peak was found on g.l.c.

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chart and the mole purity is better than 0.9997 for both solvents. Densities are 1.02870 g cm^{-3} for 1,3-dioxane and 1.02787 g cm^{-3} for 1,4-dioxane.

Excess enthalpies H^E of the mixture were measured by a flow microcalorimeter (Tokyo Riko, FMD-CD) and the precision was better than 0.3%. Details of measurement is reported elsewhere [2].

Excess heat capacities C_p^E of the mixture and the components were measured by a flow microcalorimeter which was constructed for heat capacity in our laboratory of Osaka City University. The precision was better than 0.01 J mol^{-1} K^{-1}. Details of measurements is described elsewhere [6].

Densities ρ of the mixtures and the components were measured by a vibrating-tube densimeter (Anton Paar, DMA602). The accuracy is restricted to $1.0\cdot10^{-5}$ g cm^{-3} and reproducibility is 3.010^{-6} g cm^{-3} and details of measurements are found elsewhere [7].

Sound velocities *u* of the mixtures and components were measured by sing-around method (Cho-Onpa, UVM–2) and the precision was better than 0.05 m s^{-1}. Details of measurements are reported elsewhere [5].

Isentropic compressibility, κ_S, and its excess value, κ_S^E, were estimated by the procedures described in a previous paper [5] using sound velocity *u* and density ρ.

Results and discussion

The values of excess enthalpy H^E obtained for the mixture (1,3-dioxane+1,4-dioxane) are given in Table 1. They are positive and small, only 55 J mol^{-1} at maximum. This is reasonable since the mixture is not considered a mixture of polar and non-polar liquids. However, it is reasonable the mixture is considered as usual one of isomers. As shown below the values of the other excess properties are also small to be reasonable for the mixture of isomers. Excess heat capacities C_P^E observed for the present mixture are given in Table 2. If the negative value at x=0.025 is significant, the curve is W-shaped. The values of C_P^E are so small as to be considered that the mixture is an ideal solution. However, the W-shaped curve of C_P^E, if we accepted, suggests that the mixture is not ideal nor random mixing, but some oriented structure due to dipoles may prevail [8, 9]. It may be better to consider that small H^E also is due to the cancellation of recombination of dipolar interaction broken by mixing

Table 1 Excess enthalpies of the mixture [x-1,3-dioxane+(1–x)1,4-dioxane] at 298.15 K

x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}
0.0500	13.94	0.3000	50.30	0.5500	51.02	0.8000	28.83
0.1000	25.21	0.3500	53.02	0.6000	47.96	0.8500	22.47
0.1500	34.40	0.4000	54.11	0.6500	44.28	0.9000	15.49
0.2000	41.34	0.4500	54.15	0.7000	39.94	0.9500	7.95
0.2500	46.89	0.5000	53.03	0.7500	34.67		

Table 2 Excess heat capacities of the mixture [x-1,3-dioxane+(1–x)1,4-dioxane] at 298.15 K

x	C_p^E/ J K^{-1} mol^{-1}	x	C_p^E/ J K^{-1} mol^{-1}	x	C_p^E/ J K^{-1} mol^{-1}	x	C_p^E/ J K^{-1} mol^{-1}
0.0250	–0.003	0.3000	0.028	0.6000	–0.025	0.9000	–0.059
0.0500	0.002	0.3500	0.033	0.6500	–0.040	0.9500	–0.027
0.1000	0.010	0.4000	0.011	0.7000	–0.058	0.9750	–0.022
0.1500	0.012	0.4457	0.001	0.7500	–0.075		
0.2000	0.020	0.5000	–0.014	0.8000	–0.085		
0.2500	0.033	0.5500	–0.022	0.8500	–0.082		

Table 3 Excess volumes of the mixture [x-1,3-dioxane+(1–x)1,4-dioxane] at 298.15 K

x	ρ/g cm^{-3}	V^E/cm^{-3} mol^{-1}	x	ρ/g cm^{-3}	V^E/cm^{-3} mol^{-1}
0.03645	1.027886	0.003	0.56431	1.028038	0.026
0.11860	1.027849	0.011	0.61818	1.028112	0.023
0.13821	1.027834	0.014	0.66553	1.028160	0.022
0.20935	1.027799	0.022	0.72256	1.028235	0.020
0.24710	1.027812	0.023	0.77949	1.028328	0.016
0.30643	1.027817	0.027	0.82480	1.028392	0.014
0.35616	1.027836	0.029	0.89522	1.028518	0.008
0.46399	1.027938	0.027	0.93086	1.028593	0.004
0.51370	1.027987	0.027	0.95037	1.028627	0.003

Table 4 Sound velocities, densities calculated from excess volume, and excess isentropic compressibilities of the [x-1,3-dioxane+(1–x)1,4-dioxane] at 298.15 K

x	u/ m s^{-1}	ρ_{calcd}/ cm^3 mol^{-1}	κ_S^E/ TPa^{-1}	x	u/ m s^{-1}	ρ_{calcd}/ cm^3 mol^{-1}	κ_S^E/ TPa^{-1}
0	1345.39	1.027891		0	1345.01	1.027852	
0.05009	1345.42	1.027855	0.23	0.10054	1345.33	1.027830	0.35
0.15029	1345.76	1.027816	0.47	0.20043	1345.80	1.027811	0.50
0.25020	1346.21	1.027817	0.62	0.30014	1346.27	1.027831	0.65
0.36706	1346.86	1.027863	0.68	0.40020	1346.88	1.027885	0.68
0.43013	1347.24	1.027907	0.68	0.49993	1347.46	1.027968	0.72
0.55097	1348.01	1.028021	0.65	0.60051	1348.25	1.028079	0.58
0.63730	1348.61	1.028125	0.57	0.69983	1348.95	1.028210	0.49
0.75060	1349.42	1.028285	0.43	0.80051	1349.72	1.028362	0.34
0.84998	1350.14	1.028442	0.28	0.89984	1350.34	1.028525	0.29
0.93734	1350.76	1.028590	0.16	1	1351.23	1.028700	
1	1351.26	1.028700					

The values of excess volume V^E estimated for the mixture are given in Table 3. They are positive and extremely small, less than 0.03 $\mathrm{cm^3\,mol^{-1}}$, suggesting the mixture is apparently ideal or regular solution. The values of excess isentropic compressibility κ_S^E calculated from the values of sound velocity u and density ρ_{calc} calculated by using the equation of V^E described below. For the densities of the mixtures have not been simultaneously measured when the sound velocities have been measured. The values of κ_S^E given in Table 4 are positive and so extremely small as considered to be zero. These two volumetric properties seem to emphasize as if the mixture is almost an ideal mixture. On the other hand, calorimetric results suggest the mixture is far from ideal. Both liquids are not so different from each other in consideration of molar volumes. Such situation is almost an ideal mixing or regular solution in volumetric sense. If the mixing occurs in random way, then excess heat capacity of mixture could be negative. W-shaped curve of excess heat capacity suggests the replacement is not random but fluctuated by some favourable orientation of dipole moment of 1,3-dioxane.

The curves in Figs. 1–4 are calculated from a following Redlich–Kister equation [10],

$$H^E/(\mathrm{J\,mol^{-1}})\text{ or }C_P^E/(\mathrm{J\,K^{-1}\,mol^{-1}})\text{ or }\\ V^E/(\mathrm{cm^3\,mol^{-1}})\text{ or }\kappa_S^E/\mathrm{TPa^{-1}}=x(1-x)\Sigma A_i(1-2x)^{i-1} \tag{1}$$

where x is the mole fraction of 1,3-dioxane.

The parameter A_i are estimated by the least squares method and given in Table 5, together with the standard deviations σ. The curve of C_P^E needs six parameters to represent W-shaped curve in the case that negative value of x=0.025 is significant. On the other hand, if the negative value at x=0.025 is neglected as an error permitted, three parameters are sufficient.

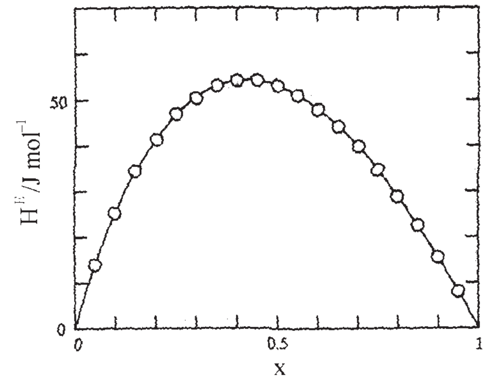

Fig. 1 Excess enthalpies of the mixture [x1,3-dioxane+(1–x) 1,4-dioxane] at 298.15 K

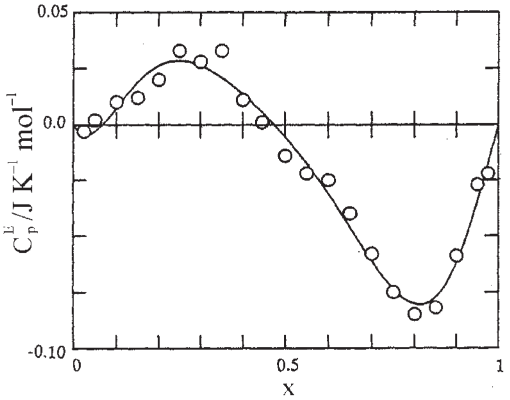

Fig. 2 Excess heat capacities of the mixture [x1,3-dioxane+(1–x) 1,4-dioxane] at 298.15 K

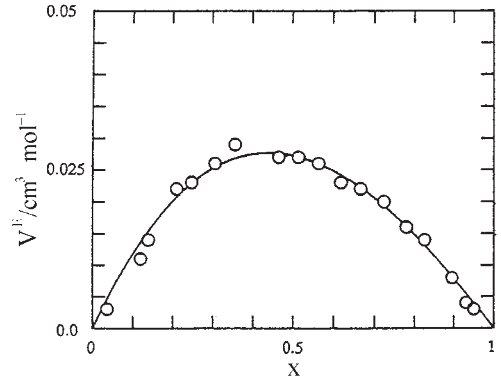

Fig. 3 Excess volumes of the mixture [x1,3-dioxane+(1–x) 1,4-dioxane] at 298.15 K

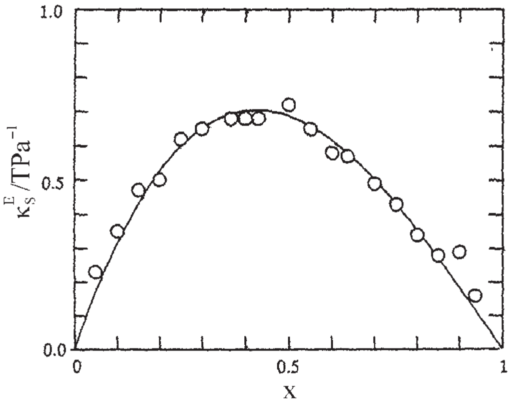

Fig. 4 Excess isentropic compressibilities of the mixture [x1,3-dioxane+(1–x) 1,4-dioxane] at 298.15 K

Table 5 Parameters of Eq. (1) for excess properties

	A_1	A_2	A_3	A_4	A_5	A_6	σ
H^E/J mol^{-1}	211.91	62.27	21.73	8.74			0.10
C_p^E/J K^{-1}mol^{-1}	–0.022	0.442	–0.366	0.642	–0.110	–0.908	0.006
V^E/cm^3 mol^{-1}	0.109	0.028					0.001
κ_S^E/TPa^{-1}	2.75	0.89					0.04

Though the excess properties of the mixture of dioxane isomers seem to show such small values as ordinary non-polar isomer mixture, it is concluded that the mixture is not regular nor randomly mixing and that local concentration is fluctuated due to orientation of bond dipole moments.

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