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Thermodynamic properties of binary mixtures {x dioxane+(1−x) non-polar liquid} at 298.15 K: measurement of excess molar heat capacity

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Abstract

Excess molar isobaric heats capacities $C_{\mathrm{P}}^{\mathrm{E}}$ of the mixtures of {x 1,3-dioxane or 1,4-dioxane+(1−x) 2,2, 4-trimethylpentane, or tetrachloroethene, or benzene} were measured at 298.15 K. $C_{\mathrm{P}}^{\mathrm{E}}$ curves for both 2,2,4-trimethylpentane systems were 'W shaped' which was discussed previously by Patterson et al. The values of $C_{\mathrm{P}}^{\mathrm{E}}$ for both tetrachloroethene systems were positive and also that of 1,3-dioxane+benzene system was positive. The values of $C_{\mathrm{P}}^{\mathrm{E}}$ of 1,4-dioxane+benzene system changed the sign from positive to negative with increase of mole fraction of dioxane. 'W-shaped' $C_{\mathrm{P}}^{\mathrm{E}}$ for the 2,2,4-trimethylpentane systems suggests the existence of non-randomness ascribed to dipolar interaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Excess heat capacity; Dioxane isomers; 2, 2,4-trimethylpentane; Tetrachloroethene; Benzene

1. Introduction

We have already reported the thermodynamic properties of cyclohexane mixtures of dioxane isomers. We found there that 1,4-dioxane shows polar property similar to 1,3-dioxane, due to local dipole moment originated to bond dipoles [1].

We have also reported the excess molar enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$, excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$ and excess thermal expansion factors α^{E} for the mixtures {x 1,3-dioxane or 1,4-dioxane+(1−x) 2,2,4-trimethylpentane, or tetrachloroethene, or benzene} at 298.15 K [2,3], in order to investigate the solution behavior of dioxane isomers in the various kinds of the following solvents different in property. 2,2,4-Trimethylpentane is typical aliphatic non-polar solvent, tetrachloroethene is non-polar and have π interactive site and bond dipoles (Cl–C), and benzene is typical aromatics showing an induced dipole–dipole interaction with polar solvents.

As a part of continuous studies on the thermodynamic properties of the dioxane isomer+non-polar solvent mixtures, we report in this report excess heat capacity $C_{\mathrm{P}}^{\mathrm{E}}$ results for the above mixtures, because it is the important thermodynamic property as a measure

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of mixing state, especially non-random mixing. We discuss on mixing states in the above mixtures in relation to various intermolecular interaction, referring to excess enthalpy.

2. Experimental

1,3- and 1,4-dioxane were purified by a fractional distillation over metal sodium and 2,2,4-trimethylpentane, tetrachloroethene and benzene were fractionally distilled. Their purities were estimated to be more than 99.99 mol% by g.l.c.

Excess heat capacity was determined by a 'direct mixing method' using a flow microcalorimeter constructed in physical chemistry laboratory of Osaka City University, in which two sample liquids were delivered into a mixing cell by a pair of piston displacement pumps. Mole fraction of the mixtures, x was determined by a ratio of flow rates of the two pumps. The details of the apparatus are described elsewhere [4]. The precision of $C_{\mathrm{P}}^{\mathrm{E}}$ and x are better than ±0.01 J K^{-1} mol^{-1} and ±0.0001, respectively.

Densities of the pure components were measured by a vibrating-tube densimeter (Anton Paar DMA 602) and shown in Table 1, together with the molar heat capacity.

3. Results and discussion

Density and molar heat capacity of pure components are given in Table 1. The heat capacity of 1,3-dioxane, 140.28 J K^{-1} mol^{-1}, is considerably small in comparison with that of 1,4-dioxane, 150.97 J K^{-1} mol^{-1} and it may be due to the dipole interaction.

The $C_{\mathrm{P}}^{\mathrm{E}}$ values obtained for the mixtures {x 1,3-dioxane or 1,4-dioxane+(1−x) 2,2,4-trimethylpentane, or tetrachloroethene, or benzene} are given in Table 2, and they are plotted in Fig. 1, together with the curves calculated by the following Redlich–Kister type fitting equation:

Table 1
Physical properties of pure component liquids at 298.15 K

	ρ (g cm^{-3})	C_{P} (J K^{-1} mol^{-1})
1,3-dioxane	1.02873	140.28
1,4-dioxane	1.02798	150.97
2,2,4-trimethylpentane	0.68753	238.55
Tetrachloroethene	1.61432	146.49
Benzene	0.87365	135.76

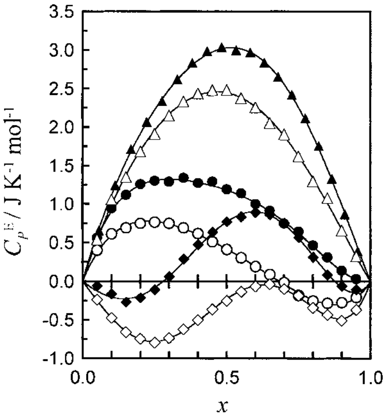

Fig. 1. Excess isobaric heat capacities of the mixtures at 298.15 K. ◆: 1,3-dioxane+2,2,4-trimethylpentane, ◇: 1,4-dioxane+2,2,4-trimethylpentane, ▲: 1,3-dioxane+tetrachloroethene, △: 1,4-dioxane+tetrachloroethene, ●: 1,3-dioxane+benzene and ○: 1,4-dioxane+benzene.

$$C_{\mathrm{P}}^{\mathrm{E}} = x(1-x)\sum A_i(1-2x)^{i-1} \qquad (1)$$

where x is the mole fraction of dioxanes, and the parameters A_i and estimated standard errors calculated by least-squares method are given in Table 3.

3.1. The 1,3- or 1,4-dioxane+2,2,4-trimethylpentane systems

As shown in Fig. 1, the curves of $C_{\mathrm{P}}^{\mathrm{E}}$ of these systems are typical 'W-shaped' curve and show characteristic concentration dependence. The curve of 1,3-dioxane system shifts more positive than that of 1,4-dioxane system.

The values of $H_{\mathrm{m}}^{\mathrm{E}}$ of both systems are large and positive; 1627 J mol^{-1} for the 1,3-dioxane system and 1675 J mol^{-1} for the 1,4-dioxane system at x=0.5 [2]. Large and positive $H_{\mathrm{m}}^{\mathrm{E}}$ of 1,3-dioxane system is due to the breaking of the dipole–dipole interaction in pure state of dioxane on the mixing with 2,2,4-trimethylpentane. The 1,4-dioxane system shows larger $H_{\mathrm{m}}^{\mathrm{E}}$ than 1,3-dioxane one in spite of the non-polarity of 1,4-dioxane and then no contribution from the dipolar–dipolar interaction. It suggests that 1,4-dioxane

Table 2
Excess isobaric heat capacities of dioxane isomers+non-polar liquid mixtures 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 1,3-dioxane+(1−x) 2,2,4-trimethylpentane					
0.0500	−0.061	0.4000	0.474	0.7500	0.567
0.1000	−0.163	0.4500	0.634	0.8000	0.314
0.1500	−0.268	0.5000	0.771	0.8500	0.085
0.2000	−0.213	0.5500	0.835	0.9000	−0.060
0.2500	−0.110	0.6000	0.891	0.9500	−0.104
0.3000	0.063	0.6500	0.862		
0.3500	0.288	0.7000	0.751		
x 1,4-dioxane+(1−x) 2,2,4-trimethylpentane					
0.0500	−0.235	0.4000	−0.499	0.7500	−0.180
0.1000	−0.474	0.4500	−0.359	0.8000	−0.339
0.1500	−0.658	0.5000	−0.248	0.8500	−0.432
0.2000	−0.744	0.5500	−0.133	0.9000	−0.507
0.2500	−0.794	0.6000	−0.065	0.9500	−0.365
0.3000	−0.735	0.6500	−0.033		
0.3500	−0.623	0.7000	−0.099		
x 1,3-dioxane+(1−x) tetrachloroethene					
0.0567	0.650	0.4322	2.981	0.7740	2.110
0.1126	1.240	0.4829	3.029	0.8204	1.754
0.1677	1.711	0.5331	2.994	0.8661	1.327
0.2220	2.063	0.5825	2.963	0.9113	0.863
0.2756	2.331	0.6313	2.833	0.9559	0.386
0.3285	2.614	0.6795	2.647		
0.3807	2.828	0.7271	2.415		
x 1,4-dioxane+(1−x) tetrachloroethene					
0.0500	0.541	0.4000	2.438	0.7500	1.624
0.1000	1.059	0.4500	2.482	0.8000	1.298
0.1500	1.351	0.5000	2.481	0.8500	1.079
0.2000	1.685	0.5500	2.377	0.9000	0.661
0.2500	1.912	0.6000	2.256	0.9500	0.328
0.3000	2.150	0.6500	2.055		
0.3500	2.334	0.7000	1.907		
x 1,3-dioxane+(1−x) benzene					
0.0500	0.555	0.4000	1.267	0.7500	0.635
0.1000	0.931	0.4500	1.286	0.8000	0.458
0.1500	1.113	0.5000	1.185	0.8500	0.306
0.2000	1.252	0.5500	1.134	0.9000	0.134
0.2500	1.296	0.6000	0.993	0.9500	0.025
0.3000	1.284	0.6500	0.903		
0.3500	1.334	0.7000	0.741		
x 1,4-dioxane+(1−x) benzene					
0.0500	0.405	0.4000	0.618	0.7500	−0.179
0.0998	0.614	0.4500	0.514	0.8000	−0.249
0.1500	0.693	0.5000	0.413	0.8500	−0.280
0.2000	0.750	0.5500	0.306	0.9000	−0.272
0.2500	0.766	0.6000	0.194	0.9500	−0.203
0.3000	0.752	0.6500	0.093		
0.3500	0.693	0.7000	−0.011		

Table 3
Parameters of Eq. (1) for excess heat capacities of the mixtures {x dioxane isomer+$(1-x)$ non-polar liquid at 298.15 K[a]

	A_1	A_2	A_3	A_4	s ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
1,3-dioxane+					
2,2,4-trimethylpentane	3.083	−5.006	−7.229	6.417	0.032
Tetrachloroethene	12.117	−0.820	−0.611	2.632	0.027
Benzene	4.733	2.581	1.645	4.300	0.024
1,4-dioxane+					
2,2,4-trimethylpentane	−0.901	−5.091	−6.870	8.068	0.016
Tetrachloroethene	9.792	1.501	−0.860	1.077	0.036
Benzene	1.673	4.110	0.038	3.164	0.021

[a] Units of C_P^E are $\mathrm{J\,K^{-1}\,mol^{-1}}$.

strongly interacts with each other through the local dipole moment due to bond dipole in ether group, and on mixing the breaking of the interaction produces large endothermic.

Patterson et al. [5] suggest the existence of 'non-randomness' in the mixture where its C_P^E curve is 'W-shaped' and H_m^E is more than 1000 $\mathrm{J\,mol^{-1}}$. These systems are the typical case. The non-randomness is attributed to the strong attractive dipole–dipole interaction between dioxane molecules. The non-randomness may be stronger in 1,3-dioxane system than in 1,4-dioxane system at 298.15 K.

3.2. The 1,3- or 1,4-dioxane+tetrachloroethene systems

The values of C_P^E of these systems are positive over the whole range of concentration and the curves are parabolic. On the other hand, the values of H_m^E of both systems are positive over the whole range of concentration. They are less than a third of H_m^E of 2,2,4-trimethylpentane systems 547.7 $\mathrm{J\,mol^{-1}}$ for the 1,3-dioxane system, and 431.2 $\mathrm{J\,mol^{-1}}$ for the 1,4-dioxane system [2]. It is considered that the attractive π–dipole interaction between the p electron of tetrachloroethene and the dipole of dioxane isomer depresses the H_m^E values in both the systems. The larger depression of 1,4-dioxane system may be due to the better configuration of pair formation by the interaction between the bond dipole of dioxane and tetrachloroethene (C–Cl) in comparison with 1,3-dioxane system. This attractive interaction is broken by temperature increase and shows endothermic, then C_P^E becomes positive and parabolic because of symmetry on concentration. This is agreed with the V_m^E results for these systems [3].

3.3. The 1,3- or 1,4-dioxane+benzene systems

The values of C_P^E of 1,4-dioxane system change the sign from positive to negative with the increase of x. On the other hand, those of 1,3-dioxane system are positive over the whole range of concentration and the curve, however, seems to shift the curve of 1,4-dioxane system to positive direction and disappears negative part, in supposing from the curvature of the curve at region of $x \doteqdot 1$.

The values of H_m^E of these systems are negative except for $x>0.8$ of 1,4-dioxane system [2], because of the strong attractive induced dipole–dipole interaction between benzene and 1,3- or 1,4-dioxane molecules.

In benzene rich region, the induced dipole–dipole interaction is thoroughly formed and then H_m^E tends to negative, while C_P^E tends to positive because of endothermic effect of the breaking of attractive interaction by temperature increase. In the opposite region, the dipole–dipole interaction between the dioxane molecules is broken by mixing and then H_m^E tends to positive, and C_P^E tends to negative because of randomizing of dipoles.

4. Conclusion

1,4-Dioxane is very similar to 1,3-dioxane in the view of local bond dipole, though 1,4-dioxane has no macroscopic dipole. Dipole–dipole interaction between 1,3-dioxane molecules is a little stronger than that between 1,4-dioxane molecules and then in the solvents only dispersion force acting the pair of dipole–dipole interaction remains more unbroken in the 1,3-dioxane system than in the 1,4-dioxane one. This makes H_m^E less positive in the 1,3-dioxane system than in the 1,4-dioxane one, and also makes C_P^E more positive in the 1,3-dioxane system than in the 1,4-dioxane one. In the mixture attractive interaction such as π–dipole and induced dipole–dipole interaction acting, attractive interaction due to dipole moment is stronger in the 1,3-dioxane system than in the 1,4-dioxane one. This also makes H_m^E less positive in the 1,3-dioxane system than in the 1,4-dioxane, and makes C_P^E more positive in the 1,3-dioxane system than in the 1,4-dioxane one.

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