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THERMODYNAMIC PROPERTIES OF MIXTURES OF A DIOXANONANE ISOMER + *n*-OCTANE AT 298.15 K.
Part I. Excess enthalpies and heat capacities

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ABSTRACT

Excess enthalpies H^E and isobaric heat capacities C_p^E of six mixtures of an isomer of the diethers 2, *m*- or 3, *n*-dioxanonane ($m = 5, 6, 7, 8$: $n = 6, 7$) + *n*-octane were measured at 298.15 K. The excess enthalpies of all mixtures were positive and very close to each other, being in the range 580–770 J mol^{-1} at the maximum and following the order of dipole moments of the diethers. The excess heat capacities are negative and show an anomalous dependence on concentration. The C_p^E curves for all the mixtures are flat near the minimum which suggests a fluctuation in the local density, similar to the non-randomness effect proposed by Patterson. Another feature of the C_p^E curve is a slightly positive region at low diether concentration, found only in the 2,7- 2,8- and 3,7-isomer mixtures. The positive effect is found in more or less all cases and suggests the possibility of inter- or intra-molecular dipole rearrangement caused by dilution with the hydrocarbon.

INTRODUCTION

Only a few thermodynamic studies on mixtures containing a polyether have been reported [1–4] because such compounds are not readily available. We are interested in the way in which the positions of functional groups (in this case two ether oxygen atoms) in isomers affect the thermodynamic

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properties of their mixtures. In this paper we report excess enthalpies and isobaric heat capacities of the binary mixtures of six isomers of dioxanonane (diether) with *n*-octane. The dioxanonane isomers are in two series; 2,*m*-dioxanonane ($m = 5$, 6, 7, 8), and 3,*n*-dioxanonane ($n = 6$, 7). They are not available commercially and have been prepared from the corresponding diols by Williamson synthesis.

EXPERIMENTAL

The diethers synthesized were fractionally distilled at about 50 mm Hg in spinning-band type distillation column (constructed by Central Workshop of Osaka City University). Their GLC charts (Thermon 1000 + KOH (Shimadzu) column material on the diatomite Chromosol (Shimadzu) as stationary phase) indicated purities of over 99.9 per cent. *n*-Octane was fractionally distilled in a 2-m distillation column with helical packing (Central Workshop of Osaka City University). Its purity was over 99.99 per cent (by GLC on a PEG column).

Excess enthalpies were measured by a modified LKB flow microcalorimeter, while the heat capacities of pure diethers and the excess heat capacities of mixtures were measured by a home-made flow microcalorimeter. The details of the experimental procedures have been reported earlier [5,6]. The dipole moments of the diethers were determined in dilute *n*-octane solution by the Halverstadts–Kumlers methods. A Picker vibrational densimeter (Sodev 101D) was used for the density measurements as described previously [7]. Errors are less than 0.2% in excess enthalpy and excess heat capacity measurements, while the accuracy of the densimetry is $\pm 10^{-5}$. The stabilities of the temperature-controlled baths are within ±0.0003 K.

RESULTS AND DISCUSSION

Physical properties of the pure substances, six diethers and *n*-octane, are presented in Table 1. The densities, ρ, of the six diethers are very similar, as are the dipole moments. The densities depend almost linearly on the magnitude of the dipole moments, with a standard deviation of 0.003 g cm^{-3} (Fig. 1). The dipole moments depend mainly on the weighted number of conformations of the central alkyl chain between the two ether oxygen atoms. The conformation of this is hindered, and thus the dipole moment is reduced from the expected free-rotation value, by the bulky alkyl chains substituted on both ether oxygen atoms [8]. In the case of an extremely short (< 3C) central alkyl chain, some unfavourable conformations are restricted, resulting in a larger dipole moment because of the lower number of possible conformations.

TABLE 1

Physical properties of dioxanonane isomers and *n*-octane

Isomers	ρ(g cm^{-3})	μ(Debye)	C_P(J K^{-1} mol^{-1})
2,5-	0.84116	1.56	279.1
2,6-	0.83727	1.48	279.0
2,7-	0.84116	1.63	280.4
2,8-	0.85154	1.73	279.0
3,6-	0.83307	1.50	278.2
3,7-	0.83122	1.49	285.2
Octane	0.69852	0.0	254.2

The isobaric heat capacities of all the diethers are almost the same, ranging from 279.0 to 285.2 J K^{-1} mol^{-1}, which is close to the value for *n*-nonane, 284.4 J K^{-1} mol^{-1} [9], having the same number of atoms in the chain. These results suggest either that the diether liquid compresses the volume due to the dipolar interaction but does not form a special structure in the pure liquid state, or that the structure due to dipolar interaction is not easily broken as the temperature rises.

Excess enthalpies of the mixtures are shown in Table 2, which are positive parabolic curves for all the mixtures, as seen in Fig. 2, in which the smoothed curves are represented by the following Redlich–Kister formula

$$X^{E}\ (\text{unit})^{-1} = x(1-x)\sum A_i(1-2x)^{i-1} \qquad (1)$$

for the excess functions, where x is mole fraction of the diether. Coefficients A_i are listed in Table 4. The magnitudes of the excess enthalpies follow the order of the dipole moment of the corresponding diether (Table 1). The relation of the excess enthalpy to the dipole moment of the corresponding diether is plotted in Fig. 3. This shows that the main contribution of the intermolecular interaction to excess enthalpy is possibly due to the dipolar interaction.

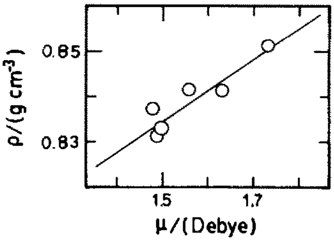

Fig. 1. Linear relation of the density, ρ, to dipole moment, μ, for dioxanonane isomers.

Excess heat capacities of the mixtures are shown in Table 3, and the smoothed curves in Fig. 2 are represented by eqn. (1). Coefficients are listed in Table 5.

TABLE 2

Excess enthalpies of *m*,*n*-dioxanonane + *n*-octane at 298.15 K

Mole fraction diether x	H^E (J mol^{-1}) (Obs.)	(Calcd.)	Diff.
x 2,5-dioxanonane + $(1-x)$ *n*-octane			
0.05001	152.5	154.3	−1.8
0.10002	289.2	288.3	0.9
0.15003	404.2	403.0	1.2
0.20004	499.4	499.3	0.1
0.25005	578.5	578.3	0.2
0.30006	639.8	640.5	−0.7
0.35006	686.4	686.8	−0.4
0.40006	717.1	717.6	−0.5
0.45006	734.0	733.7	0.3
0.50006	734.5	735.4	−0.9
0.55006	724.1	723.1	1.0
0.60005	696.0	697.0	−1.0
0.65006	658.1	657.4	0.7
0.70004	605.1	604.4	0.7
0.75005	538.5	537.9	0.6
0.80004	457.4	458.0	−0.6
0.85003	365.4	364.6	0.8
0.90002	256.5	257.3	−0.8
0.95001	134.0	135.9	−1.9
x 2,6-dioxanonane + $(1-x)$ *n*-octane			
0.05000	117.3	118.7	−1.4
0.10000	222.7	222.6	0.1
0.15000	312.6	312.5	0.1
0.20000	389.2	388.8	0.4
0.25000	452.5	452.0	0.5
0.30000	502.5	502.7	−0.2
0.35000	541.3	541.2	0.1
0.40000	568.1	567.9	0.2
0.45000	582.6	582.9	−0.3
0.50000	585.4	586.6	−1.2
0.55000	579.1	579.0	0.1
0.60000	560.7	560.3	0.4
0.65000	531.0	530.4	0.6
0.70000	489.6	489.4	0.2
0.75000	436.9	437.2	−0.3
0.80000	373.4	373.5	−0.1
0.85000	298.3	298.3	0.0
0.90000	211.1	211.2	−0.1
0.95000	111.8	111.9	−0.1

TABLE 2 (continued)

Mole fraction diether x	H^E (J mol^{-1})		
	(Obs.)	(Calcd.)	Diff.
x 2,7-dioxanonane + $(1-x)$ n-octane			
0.05000	134.1	135.4	−1.3
0.10000	253.8	254.3	−0.5
0.15000	358.1	357.3	0.8
0.20000	445.6	445.0	0.6
0.25000	518.1	517.9	0.2
0.30000	576.7	576.4	0.3
0.35000	620.7	621.0	−0.3
0.40000	651.6	652.0	−0.4
0.45000	669.2	669.7	−0.5
0.50000	673.3	674.2	−0.9
0.55000	666.4	665.7	0.7
0.60000	644.7	644.4	0.3
0.65000	610.7	610.1	0.6
0.70000	562.8	563.0	−0.2
0.75000	503.3	502.9	0.4
0.80000	429.8	429.6	0.2
0.85000	342.6	343.0	−0.4
0.90000	242.5	242.8	−0.3
0.95000	128.2	128.6	−0.4
x 2,8-dioxanonane + $(1-x)$ n-octane			
0.05000	156.8	157.6	−0.8
0.10000	293.5	294.5	−1.0
0.15000	413.6	411.9	1.7
0.20000	510.7	511.0	−0.3
0.25000	593.4	592.7	0.7
0.30000	656.3	657.8	−1.5
0.35000	708.8	707.0	1.8
0.40000	739.8	740.7	−0.9
0.45000	759.1	759.4	−0.3
0.50000	764.1	763.2	0.9
0.55000	750.6	752.5	−1.9
0.60000	727.8	727.2	0.6
0.65000	688.4	687.5	0.9
0.70000	633.3	633.3	0.0
0.75000	564.5	564.5	−0.0
0.80000	480.3	481.1	−0.8
0.85000	384.0	383.1	0.9
0.90000	270.4	270.2	0.2
0.95000	141.6	142.6	−1.0
x 3,6-dioxanonane + $(1-x)$ n-octane			
0.05000	143.5	144.4	−0.9
0.15000	379.7	378.6	1.1
0.25000	545.5	545.3	0.2
0.35000	648.8	650.2	−1.4
0.45000	698.1	697.7	0.4

TABLE 2 (continued)

Mole fraction diether x	H^E (J mol^{-1}) (Obs.)	(Calcd.)	Diff.
x 3,6-dioxanonane + $(1-x)$ n-octane			
0.50000	700.8	700.8	−0.0
0.55000	690.9	690.6	0.3
0.65000	631.1	630.9	0.2
0.75000	518.8	518.7	0.1
0.85000	353.1	353.3	−0.2
0.95000	132.0	132.3	−0.3
x 3,7-dioxanonane + $(1-x)$ n-octane			
0.05000	121.1	122.7	−1.6
0.15000	324.5	323.9	0.6
0.25000	470.2	469.5	0.7
0.35000	562.6	562.9	−0.3
0.45000	606.4	606.6	−0.2
0.50000	610.3	610.5	−0.2
0.55000	602.5	602.6	−0.1
0.65000	552.1	551.7	0.4
0.75000	454.1	454.2	−0.1
0.85000	309.4	309.3	0.1
0.95000	115.6	115.7	−0.1

As seen in Fig. 4, the excess heat capacities are negative as a whole and their minima depend on the length of the central alkyl chain between the ether oxygen atoms. This suggests that the excess heat capacities depend on the conformation change of the methylene groups between the ether oxygen

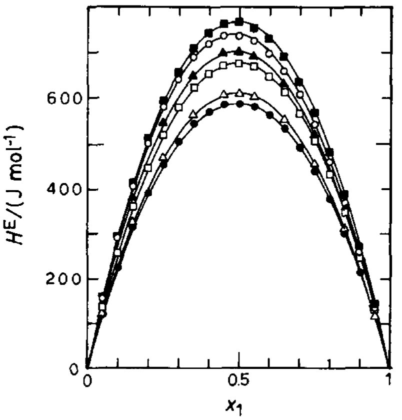

Fig. 2. Excess enthalpies of x dioxanonane + $(1-x)$ n-octane: ○, 2,5-dioxanonane + n-octane; ●, 2,6-dioxanonane + n-octane; □, 2,7-dioxanonane + n-octane; ■, 2,8-dioxanonane + n-octane; ▲, 3,6-dioxanonane + n-octane; △, 3,7-dioxanonane + n-octane.

TABLE 3

Excess heat capacities of an isomer of dioxanonane + n-octane at 298.15 K

Mole fraction diether x	C_P^E(J K^{-1} mol^{-1})		
	(Obs.)	(Calcd.)	Diff.
x 2,5-dioxanonane + $(1-x)$ n-octane			
0.02500	−0.027	−0.045	0.018
0.05000	−0.123	−0.133	0.010
0.10001	−0.388	−0.371	−0.017
0.15001	−0.621	−0.618	−0.003
0.20001	−0.840	−0.832	−0.008
0.25001	−0.980	−1.003	0.023
0.30001	−1.156	−1.134	−0.022
0.35002	−1.206	−1.235	0.029
0.40002	−1.329	−1.315	−0.014
0.45002	−1.369	−1.378	0.009
0.50002	−1.448	−1.423	−0.025
0.55002	−1.437	−1.446	0.009
0.60002	−1.450	−1.443	−0.007
0.70002	−1.330	−1.351	0.021
0.80001	−1.169	−1.156	−0.013
0.90000	−0.838	−0.828	−0.010
0.95000	−0.515	−0.528	0.013
0.97500	−0.297	−0.303	0.006
x 2,6-dioxanonane + $(1-x)$ n-octane			
0.02500	−0.025	−0.022	−0.003
0.05000	−0.079	−0.082	0.003
0.10000	−0.254	−0.262	0.008
0.15000	−0.463	−0.462	−0.001
0.20000	−0.665	−0.646	−0.019
0.30000	−0.918	−0.932	0.014
0.40000	−1.115	−1.127	0.012
0.45000	−1.196	−1.197	0.001
0.50000	−1.263	−1.247	−0.016
0.55000	−1.284	−1.273	−0.011
0.60000	−1.281	−1.273	−0.008
0.65000	−1.226	−1.246	0.020
0.70000	−1.185	−1.196	0.011
0.75000	−1.120	−1.127	0.007
0.80000	−1.058	−1.040	−0.018
0.85000	−0.938	−0.931	−0.007
0.90000	−0.773	−0.773	0.000
0.95000	−0.486	−0.503	0.017
0.97500	−0.297	−0.291	−0.006

atoms induced by dilution with n-octane. The curves are, however, not simple parabolic dependences on concentration. They tend to flatten near the minimum, because of fluctuations in local concentration, similar to the

TABLE 3 (continued)

Mole fraction diether x	C_P^E(J K^{-1} mol^{-1})		
	(Obs.)	(Calcd.)	Diff.
x 2,7-dioxanonane + (1 − x) *n*-octane			
0.02500	0.051	0.052	−0.001
0.05000	0.022	0.029	−0.007
0.10000	−0.112	−0.118	0.006
0.15000	−0.287	−0.293	0.006
0.20000	−0.454	−0.448	−0.006
0.25000	−0.574	−0.576	0.002
0.29999	−0.696	−0.687	−0.009
0.35000	−0.789	−0.789	0.000
0.40000	−0.877	−0.883	0.006
0.44999	−0.953	−0.963	0.010
0.50000	−1.024	−1.021	−0.003
0.55000	−1.063	−1.053	−0.010
0.59999	−1.059	−1.059	0.000
0.64999	−1.045	−1.044	−0.001
0.70000	−1.012	−1.013	0.001
0.75000	−0.961	−0.972	0.011
0.80000	−0.920	−0.914	−0.006
0.85000	−0.823	−0.821	−0.002
0.90000	−0.661	−0.660	−0.001
0.95000	−0.399	−0.394	−0.005
0.97500	−0.202	−0.213	0.011
x 2,8-dioxanonane + (1 − x) *n*-octane			
0.02500	0.029	0.029	0.000
0.05000	0.007	0.009	−0.002
0.09999	−0.104	−0.106	0.002
0.14999	−0.241	−0.249	0.008
0.19999	−0.391	−0.380	−0.011
0.24999	−0.487	−0.484	−0.003
0.29999	−0.572	−0.566	−0.006
0.34999	−0.615	−0.632	0.017
0.39999	−0.674	−0.689	0.015
0.44998	−0.758	−0.738	−0.020
0.49999	−0.783	−0.778	−0.005
0.54999	−0.815	−0.806	−0.009
0.59999	−0.806	−0.817	0.011
0.64999	−0.799	−0.809	0.010
0.69999	−0.790	−0.787	−0.003
0.79999	−0.722	−0.715	−0.007
0.90000	−0.582	−0.583	0.001
0.95000	−0.394	−0.403	0.009
0.97500	−0.249	−0.240	−0.009

TABLE 3 (continued)

Mole fraction diether x	C_P^E(J K^{-1} mol^{-1})		
	(Obs.)	(Calcd.)	Diff.
x 3,6-dioxanonane + $(1-x)$ n-octane			
0.02500	−0.050	−0.064	0.014
0.05000	−0.168	−0.173	0.005
0.10000	−0.461	−0.456	−0.005
0.20000	−1.042	−1.024	−0.018
0.30000	−1.410	−1.431	0.021
0.40000	−1.679	−1.687	0.008
0.45000	−1.776	−1.771	−0.005
0.50000	−1.835	−1.825	−0.010
0.55000	−1.862	−1.848	−0.014
0.60000	−1.837	−1.836	−0.001
0.70000	−1.667	−1.702	0.035
0.80000	−1.452	−1.429	−0.023
0.90000	−0.990	−0.979	−0.011
0.95000	−0.581	−0.603	0.022
x 3,7-dioxanonane + $(1-x)$ n-octane			
0.02500	0.028	0.035	−0.007
0.05000	0.021	0.003	0.018
0.15000	−0.421	−0.402	−0.019
0.25000	−0.808	−0.819	0.011
0.34999	−1.119	−1.126	0.007
0.44999	−1.352	−1.347	−0.005
0.49999	−1.434	−1.422	−0.012
0.54999	−1.471	−1.467	−0.004
0.59999	−1.463	−1.476	0.013
0.65000	−1.445	−1.448	0.003
0.74999	−1.300	−1.298	−0.002
0.85000	−1.068	−1.063	−0.005
0.95000	−0.575	−0.581	0.006

so-called non-randomness effect proposed by Patterson et al. [10]. Another feature of the C_P^E curve is a very small positive region at low diether concentration, found in three mixtures of the 2,7-, 2,8-, and 3,7-isomers.

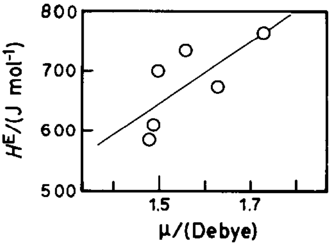

Fig. 3. Relation of the excess enthalpy, H^E, to dipole moment, μ, for dioxanonane isomers.

TABLE 4

Coefficients of eq. (1) for excess enthalpies of x n,m-dioxanonane + $(1-x)$ n-octane mixtures at 298.15 K

Coefft.	n,m					
	2,5-	2,6-	2,7-	2,8-	3,6-	3,7-
A_1	2941.6	2346.3	2696.8	3052.9	2803.3	2442.0
A_2	214.5	79.3	79.9	138.9	141.6	81.9
A_3	139.4	99.6	100.8	132.3	136.1	84.5
A_4	–	–	–	46.3	–	–
s	1.0	0.5	0.6	1.1	0.8	0.7

TABLE 5

Coefficients of eq. (1) for excess heat capacities of x n,m-dioxanonane + $(1-x)$ n-octane mixtures at 298.15 K

Coefft.	n,m					
	2,5-	2,6-	2,7-	2,8-	3,6-	3,7-
A_1	−5.693	−4.988	−4.084	−3.114	−7.301	−5.690
A_2	1.392	1.539	1.831	1.379	1.578	2.453
A_3	−1.357	−0.250	1.238	−0.522	−0.970	0.471
A_4	−1.719	−0.753	−0.092	−1.541	−0.772	−1.835
A_5	−0.251	−1.477	−7.643	−0.925	−0.125	−1.186
A_6	7.038	6.076	4.873	7.135	6.220	8.935
A_7	–	–	8.009	–	–	–
s	0.019	0.014	0.008	0.011	0.022	0.014

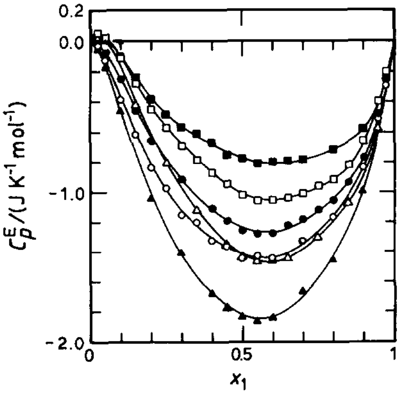

Fig. 4. Excess heat capacities of x dioxanonane + $(1-x)$ n-octane: ○, 2,5-dioxanonane + n-octane; ●, 2,6-dioxanonane + n-octane; □, 2,7-dioxanonane + n-octane; ■, 2,8-dioxanonane + n-octane; ▲, 3,6-dioxanonane + n-octane; △, 3,7-dioxanonane + n-octane.

These isomers have a long central alkyl chain and short terminal alkyl chains. It is considered that in dilute solution the conformation of the central carbon chain changes and the molecule rearranges to a favoured form for construction of stable pairs of dipoles, and the longer this chain then the larger is the possibility of construction of such stable pairs.

It is concluded that the differences in the thermal properties of the mixtures are almost entirely caused by the dipole moments of the diether molecules, which are resultants of the weighted contributions of the conformations of the central alkyl chain.

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