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Thermodynamic properties of 2,5,8-trioxanonane + n-octane mixture at 298.15 K [α]

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Abstract

Thermodynamic properties of the 2,5,8-trioxanonane + n-octane mixture are studied at 298.15 K. The excess enthalpy H^E and excess heat capacity C_p^E are measured. The excess volume V^E is estimated from density measurement, and excess isentropic and isothermal compressibilities, κ_S^E and κ_T^E, are obtained from measurements of density and speed of sound. Excess enthalpy and excess volume are very large and positive and exhibit parabolic behavior, whereas excess heat capacity and excess compressibilities show anomalous dependence on concentration. Fluctuations of local concentration, the so-called non-randomness effect proposed by Patterson et al., are obviously observed. The thermodynamic properties of the mixture have been compared with those of dioxanonane isomer + n-octane and 2,5,8-trioxanonane + n-heptane mixtures.

INTRODUCTION

We have taken an interest in the effects that the number and positions of functional groups (in this case ether oxygen atoms) of tri- or di-oxanonane isomers have on the thermodynamic properties of mixtures. In previous papers [1,2] we have reported excess enthalpies, H^E, excess heat capacities, C_p^E, excess volumes, V^E, and excess isentropic and isothermal compressibilities, κ_S^E and κ_T^E, of binary mixtures of a dioxanonane isomer + n-octane. The excess enthalpies and volumes are positive and parabolic; the excess heat

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capacities and a few of the excess isothermal or isentropic compressibilities, however, show anomalous dependence on concentration. In this paper, we report excess enthalpy, excess volume, excess heat capacity, and excess isentropic and isothermal compressibilities of 2,5,8-trioxanonane (triether) + *n*-octane mixture, and compare them with the corresponding properties of binary mixtures of a dioxanonane isomer (diether) + *n*-octane.

EXPERIMENTAL

2,5,8-Trioxanonane (triether) was not purified further because the curve from its gas chromatography [column: stationary phase Thermon 1000 + KOH (Shimadzu) on Chromosol diatomite (Shimadzu)] showed its purity to be more than 99.9%. *n*-Octane and *n*-heptane were fractionally distilled with a 2-m distillation column (constructed by the Central Workshop of Osaka City University), and were shown by gas chromatography on a PEG column to be more than 99.99% pure.

The excess enthalpy was measured with an LKB flow microcalorimeter; details are given elsewhere [3]. The heat capacities of the pure substances and the excess heat capacities of the mixtures were measured by using a home-made flow microcalorimeter, as described elsewhere [4]. The density was measured with a vibrational densimeter (Anton Paar DMA 602); details are given in Ref. 5. The speed of sound was measured by the Sing around method (Cho-Onpa Kogyo Co., UVM-2); details are given elsewhere [6]. Errors of the measurements were less than 0.2% for excess enthalpy and 0.01% for C_p^E/C_p, and within $\pm 10^{-5}$ for densimetry; the accuracy of measuring the speed of sound was ± 0.6 m s^{-1} and the reproducibility was ± 0.3 m s^{-1}.

RESULTS AND DISCUSSION

Physical properties of the triether and the hydrocarbons are shown in Table 1. The dipole moment μ of the triether was measured on a dilute solution in *n*-octane.

The observed values of excess enthalpies of the triether + *n*-octane mixture and those calculated by a smoothed function are reported in Table 2, along with the difference between them. The smoothed function is given by

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

for all the excess properties. The excess volume, the excess heat capacity and the excess isentropic and isothermal compressibility are given in Tables 3, 4, 5 and 6, respectively. Coefficients of the smoothed function are given in Table 7, along with the standard deviation s. The excess enthalpies H^E of

TABLE 1

Thermodynamic properties of 2,5,8-trioxanonane, *n*-octane and *n*-heptane

Property	2,5,8-Trioxanonane	*n*-Octane	*n*-Heptane
ρ (g cm^{-3})	0.93882	0.69855	0.67953
μ Debye	1.87	0.0	0.0
C_p (J K^{-1} mol^{-1})	276.9	254.2	224.7
α (kK^{-1})	1.03	1.15	1.22
u (m s^{-1})	1279.5	1172.9	1131.3
κ_S (TPa^{-1})	650.6	1040.5	1149.8
κ_T (TPa^{-1})	813.9	1294.2	1440.9

Note: ρ = density; u = speed of sound.

the diether isomer + *n*-octane mixtures are parabolic endotherms; their maximum values are 680–850 J mol^{-1} and follow the order of the dipole moments of the dioxanonane isomers [1]. However, H^E values of the triether +*n*-octane mixture reached 1680 J mol^{-1}, twice those of the diether mixtures, as may be seen, with previous results, in Fig. 1. The H^E curve of the triether mixture slightly changes curvature in both the regions of extreme

TABLE 2

Excess enthalpies of x 2,5,8-trioxanonane + $(1-x)$ *n*-octane at 298.15 K

x	H^E (obs) (J mol^{-1})	H^E (calc) (J mol^{-1})	Difference (J mol^{-1})
0.02500	175	181	−6
0.05000	357	358	−1
0.05000	358	358	−0
0.10000	692	684	8
0.15000	954	956	−2
0.20000	1169	1173	−4
0.25000	1342	1343	−1
0.30000	1475	1473	2
0.35000	1571	1569	2
0.40000	1638	1635	3
0.45000	1670	1672	−2
0.50000	1680	1680	0
0.55000	1656	1659	−3
0.60000	1609	1608	1
0.65000	1531	1529	2
0.70000	1422	1422	0
0.75000	1285	1284	1
0.80000	1112	1114	−2
0.85000	905	905	0
0.90000	651	651	−0
0.95000	349	348	1

TABLE 3

Excess volumes of x 2,5,8-trioxanonane + $(1-x)$ *n*-octane or *n*-heptane at 298.15 K

x	V^E (obs) ($cm^3\ mol^{-1}$)	V^E (calc) ($cm^3\ mol^{-1}$)	Difference ($cm^3\ mol^{-1}$)
x 2,5,8-trioxanonane + $(1-x)$ *n*-octane			
0.05002	0.2714	0.2701	0.0013
0.09894	0.4889	0.4874	0.0015
0.15011	0.6701	0.6715	−0.0014
0.19922	0.8100	0.8119	−0.0019
0.24952	0.9238	0.9233	0.0005
0.29858	1.0041	1.0040	0.0001
0.34935	1.0614	1.0616	−0.0002
0.39943	1.0951	1.0950	0.0001
0.40039	1.0968	1.0954	0.0014
0.45237	1.1068	1.1073	−0.0005
0.49254	1.1034	1.1018	0.0016
0.54617	1.0744	1.0754	−0.0010
0.59539	1.0324	1.0326	−0.0002
0.64821	0.9665	0.9672	−0.0007
0.69119	0.8977	0.8992	−0.0015
0.75243	0.7791	0.7790	0.0001
0.79447	0.6811	0.6803	0.0008
0.84539	0.5444	0.5428	0.0016
0.89698	0.3833	0.3829	0.0004
0.92177	0.2999	0.2986	0.0013
0.94472	0.2169	0.2161	0.0008
0.96421	0.1380	0.1427	−0.0047
0.97403	0.1025	0.1046	−0.0021
x 2,5,8-trioxanonane + $(1-x)$ *n*-heptane			
0.10064	0.4424	0.4443	−0.0019
0.19620	0.7066	0.7048	0.0018
0.30024	0.8615	0.8615	0.0000
0.39416	0.9190	0.9193	−0.0003
0.49349	0.9131	0.9126	0.0005
0.59342	0.8429	0.8449	−0.0020
0.68889	0.7265	0.7264	0.0001
0.79464	0.5384	0.5351	0.0033
0.89947	0.2831	0.2860	−0.0029

concentration. The H^E of the 2,5,8-trioxanonane + *n*-heptane mixture reported by Kimura et al. [7] hardly differs from that for the *n*-octane mixture, as also illustrated in Fig. 1.

An estimation of excess enthalpy by the Kehiaian group surface interaction theory [8] is in good agreement with the experimental results. The parameters required in the estimation process, molecular volume r_i and surface area q_i referred to methane, surface fraction of the ether oxygen atom in each molecule α_{ei}, and the parameter $C_{2,ae}$ in the molar interchange

TABLE 4

Excess heat capacities of x 2,5,8-trioxanonane + (1-x) n-octane at 298.15 K

x	C_p^E (obs) ($J\,K^{-1}\,mol^{-1}$)	C_p^E (calc) ($J\,K^{-1}\,mol^{-1}$)	Difference ($J\,K^{-1}\,mol^{-1}$)
0.05000	−0.242	−0.243	0.001
0.09999	−0.487	−0.491	0.004
0.14999	−0.646	−0.647	0.001
0.19999	−0.700	−0.694	−0.006
0.24999	−0.673	−0.661	−0.012
0.29999	−0.583	−0.590	0.007
0.34999	−0.506	−0.522	0.016
0.39998	−0.487	−0.488	0.001
0.44998	−0.502	−0.501	−0.001
0.49999	−0.574	−0.560	−0.014
0.54999	−0.665	−0.656	−0.009
0.59999	−0.762	−0.772	0.010
0.64999	−0.897	−0.892	−0.005
0.69999	−0.988	−1.003	0.015
0.74999	−1.093	−1.098	0.005
0.79999	−1.167	−1.165	−0.002
0.84999	−1.210	−1.181	−0.029
0.89999	−1.066	−1.089	0.023
0.95000	−0.770	−0.769	−0.001

energy between alkyl group (CH_3– or –CH_2–) and ether group (–O–), $h^\circ = C_{2,ae}RT$, are taken from Kehiaian's table [8]; they are given again in Table 8. The inductive process is ignored and the resultant representation for H^E in this case is

$$H^E = x(1-x)q_1q_2\alpha_{e1}^2C_{2,ae}RT/[q_2 + (q_1 - q_2)x] \tag{2}$$

where x is the mole fraction of the polyether and suffixes 1 and 2 indicate polyether and hydrocarbon, respectively. This equation changes to the Myers–Scott type

$$H^E = x(1-x)\mathrm{A}/[1 - \mathrm{B}(1-2x)] \tag{3}$$

$$\mathrm{A} = [2q_1q_2\alpha_{e1}^2C_{2,ae}RT/(q_1 + q_2)] \tag{4}$$

$$\mathrm{B} = (q_1 - q_2)/(q_1 + q_2) \tag{5}$$

Furthermore, the expansion of the denominator leads to the Redlich–Kister type equation (1). The first coefficient is represented by A, and the second by AB, and then $\mathrm{AB}^2/2$, and so on. The coefficient A calculated for the triether + n-octane mixture, 7292.5, agrees with the experimental value, 6720, and that calculated for the diether + n-octane mixture, 2947.9, also agrees with the mean value, 2714, of the first coefficients obtained for six diether mixtures [1].

TABLE 5

The density ρ, speed of sound u, and isentropic compressibility κ_S of x 2,5,8-trioxanonane + $(1-x)$ *n*-octane or *n*-heptane at 298.15 K

x	ρ (g cm^{-3})	u (m s^{-1})	κ_S (TPa^{-1})	κ_S^E (obs) (TPa^{-1})	κ_S^E (calc) (TPa^{-1})	Difference (TPa^{-1})
x 2,5,8-trioxanonane + $(1-x)$ *n*-octane						
0.00000	0.698587	1172.83	1040.50			
0.05002	0.707974	1171.03	1030.03	5.49	5.34	0.15
0.09894	0.717451	1170.34	1017.61	9.15	9.21	−0.06
0.15011	0.727675	1170.35	1003.30	12.00	12.10	−0.10
0.19922	0.737747	1170.94	988.61	14.10	13.97	0.13
0.24952	0.748316	1172.52	972.01	15.03	15.15	−0.12
0.29858	0.758888	1174.49	955.26	15.72	15.72	0.00
0.34935	0.770088	1177.16	937.10	15.96	15.83	0.13
0.40039	0.781602	1180.72	917.74	15.47	15.54	−0.07
0.96421	0.928143	1269.86	668.15	0.83	0.79	0.04
1.00000	0.938822	1279.47	650.65			
0.00000	0.698546	1172.88	1040.63			
0.39943	0.781359	1180.69	918.07	15.49	15.55	−0.06
0.49254	0.803042	1188.56	881.49	14.30	14.26	0.04
0.54617	0.815957	1194.16	859.43	13.20	13.16	0.04
0.59539	0.828064	1200.09	838.51	11.91	11.96	−0.05
1.00000	0.938817	1279.58	650.56			
0.00000	0.698546	1172.96	1040.50			
0.64821	0.841338	1207.08	815.76	10.58	10.51	0.07
0.69119	0.852391	1213.53	796.63	9.23	9.24	−0.01
0.75243	0.868506	1223.76	768.84	7.29	7.30	−0.01
0.79447	0.879841	1231.56	749.35	5.89	5.93	−0.04
0.84539	0.893881	1241.90	725.35	4.20	4.27	−0.07
0.89698	0.908478	1253.29	700.78	2.67	2.65	0.02
0.94472	0.922319	1264.87	677.68	1.30	1.28	0.02
0.97403	0.931004	1272.43	663.40	0.56	0.55	0.01
1.00000	0.938781	1279.44	650.73			
x 2,5,8-trioxanonane + $(1-x)$ *n*-heptane						
0.00000	0.679528	1131.33	1149.78			
0.10064	0.702783	1133.05	1108.35	3.81	3.77	0.04
0.19620	0.725638	1138.02	1064.10	3.67	3.68	−0.01
0.30024	0.751256	1146.49	1012.67	1.46	1.51	−0.05
0.39416	0.774915	1156.64	964.61	−1.12	−1.11	−0.01
0.49349	0.800432	1169.83	912.91	−3.67	−3.76	0.09
0.59342	0.826626	1185.82	860.31	−5.80	−5.77	−0.03
0.68889	0.852120	1203.55	810.17	−6.77	−6.76	−0.01
0.79464	0.880947	1226.26	754.89	−6.54	−6.49	−0.05
0.89947	0.910223	1251.86	701.04	−4.33	−4.39	0.06
1.00000	0.938832	1279.49	650.63			

TABLE 6

Isothermal compressibilities, κ_T, and excess ones, κ_T^E, of x 2,5,8-trioxanonane + n-octane or n-heptane at 298.15 K

x	κ_T (TPa^{-1})	κ_T^E (obs) (TPa^{-1})	κ_T^E (calc) (TPa^{-1})	Difference (TPa^{-1})
x 2,5,8-trioxanonane + (1 − x) n-octane				
0.00000	1294.3			
0.05002	1279.3	6.1	6.1	0.0
0.09894	1262.6	10.4	10.4	−0.0
0.15011	1243.7	13.6	13.7	−0.1
0.19922	1224.4	15.9	15.8	0.1
0.24952	1203.1	17.0	17.1	−0.1
0.29858	1181.7	17.7	17.7	0.0
0.34935	1158.8	17.9	17.8	0.1
0.40039	1134.6	17.4	17.5	−0.1
0.96421	834.8	1.4	1.3	0.1
1.00000	813.9			
0.00000	1294.3			
0.39943	1135.1	17.4	17.5	−0.1
0.49254	1090.0	16.2	16.2	0.0
0.54617	1063.1	15.1	15.0	0.1
0.59539	1037.8	13.8	13.8	−0.0
1.00000	813.8			
0.00000	1294.2			
0.64821	1010.4	12.5	12.4	0.1
0.69119	987.5	11.1	11.1	0.0
0.75243	954.3	9.0	9.0	−0.0
0.79447	931.1	7.5	7.6	−0.1
0.84539	902.7	5.6	5.7	−0.1
0.89698	873.6	3.8	3.8	0.0
0.94472	846.2	2.1	2.0	0.1
0.97403	829.1	1.0	0.9	0.1
1.00000	814.0			
x 2,5,8-trioxanonane + (1 − x) n-heptane				
0.00000	1440.9			
0.10064	1385.3	5.7	5.7	0.0
0.19620	1327.0	6.1	6.1	0.0
0.30024	1260.6	3.8	3.9	−0.1
0.39416	1199.4	1.0	1.0	−0.0
0.49349	1134.6	−1.8	−1.9	0.1
0.59342	1069.5	−4.0	−4.0	0.0
0.68889	1008.0	−5.2	−5.2	−0.0
0.79464	940.6	−5.3	−5.2	−0.1
0.89947	875.1	−3.6	−3.7	0.1
1.00000	813.9			

TABLE 7

Coefficients of smoothed equation and estimated standard deviation s of the properties of x 2,5,8-trioxanonane + $(1-x)$ n-octane or n-heptane at 298.15 K

X^E	A_1	A_2	A_3	A_4	A_5	A_6	A_7	s
x 2,5,8-trioxanonane + $(1-x)$ n-octane								
H^E	6720	266	884	372	1507	−683	−1860	3.4
V^E	4.3975	0.6959	0.6336	0.2013				0.0016
C_p^E	−2.242	3.202	−9.529	−6.659	−1.061	12.716		0.014
κ_S^E	56.48	38.09	14.48	13.45				0.08
κ_T^E	64.1	39.1	23.1	13.0				0.09
x 2,5,8-trioxanonane + $(1-x)$ n-heptane								
V^E	3.6399	0.8413	0.6209	0.3948				0.0024
κ_S^E	−15.66	47.27	19.16	14.33				0.06
κ_T^E	−8.1	50.8	29.9	21.7				0.06

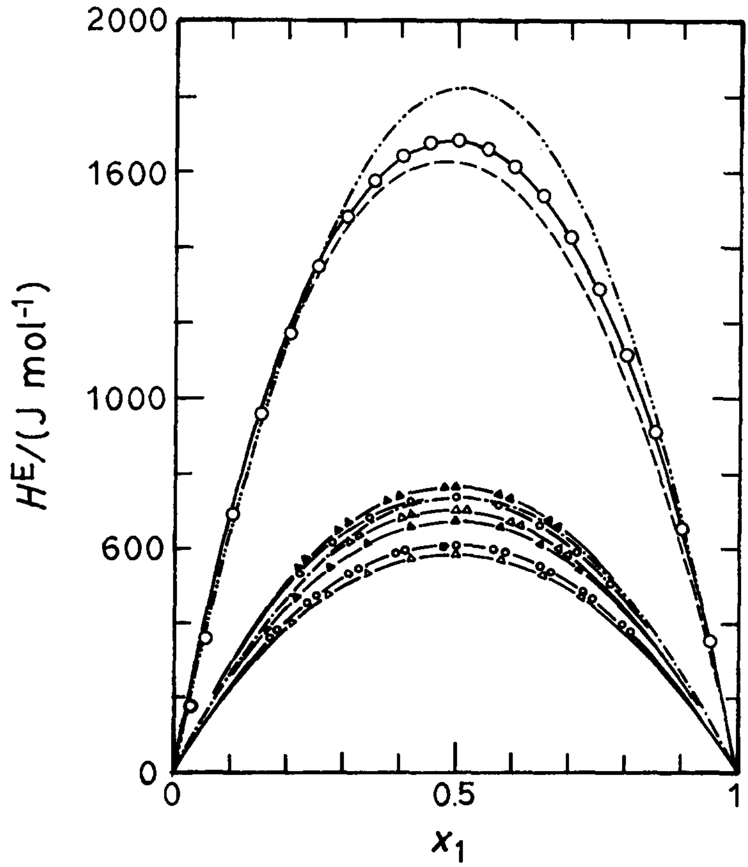

Fig. 1. Excess enthalpy of x polyether + $(1-x)$ n-octane or n-heptane: ○, 2,5,8-trioxanonane + n-octane; — — —, 2,5,8-trioxanonane + n-heptane [7]; · · — · · — · ·, calculated for trioxanonane + n-octane by surface group contribution theory; ·—·—·, calculated for dioxanonane + n-octane by surface group contribution theory; o, 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; oo, 3,7-dioxanonane + n-octane.

TABLE 8

Parameters required for surface group contribution treatment. From Kehiaian et al. [8]

Substance	r_i	q_i	α_{ei}
Trioxanonane	4.6355	3.9448	0.1573
Dioxanonane	5.0170	4.2035	0.0984
n-Octane	5.1822	4.2552	0.0
Interchange energy parameter $C_{2,ae} = 29.04$			

The excess volume V^E of the triether + n-octane mixture is positive and parabolic, and the maximum value is approximately 1.1 cm^3 mol^{-1}, while those of the diether isomer + n-octane mixtures are about half of this, as seen in Fig. 2. The maximum values are about 0.6 cm^3 mol^{-1} for the 3,n-isomer mixtures and about 0.5 cm^3 mol^{-1} for the 2,n-isomer ones [2].

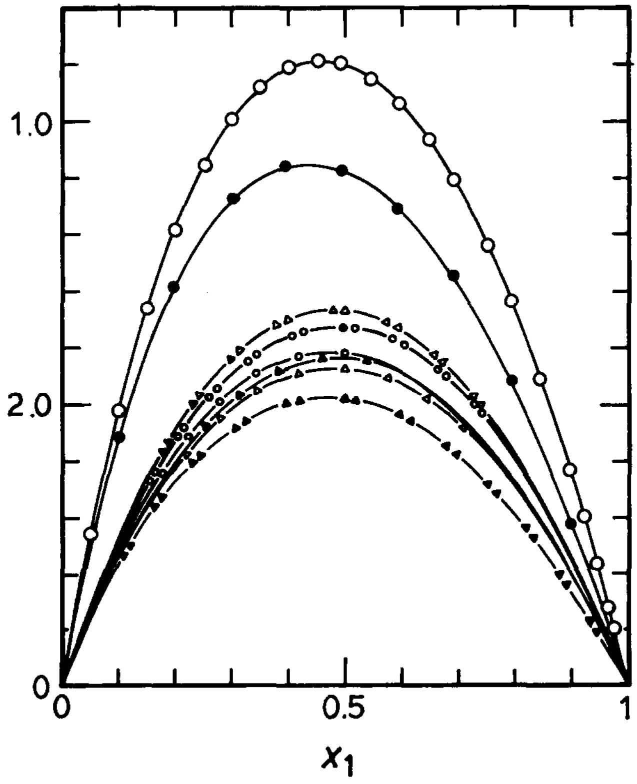

Fig. 2. Excess volume of x polyether + $(1-x)$ n-octane or n-heptane: ○, 2,5,8-trioxanonane + n-octane; ●, 2,5,8-trioxanonane + n-heptane; ○, 2,5-dioxanonane + n-octane; △, 2,6-dioxanonane + n-octane; ▲, 2,7-dioxanonane + n-octane; ▲▲, 2,8-dioxanonane + n-octane; △△, 3,6-dioxanonane + n-octane; ○○, 3,7-dioxanonane + n-octane.

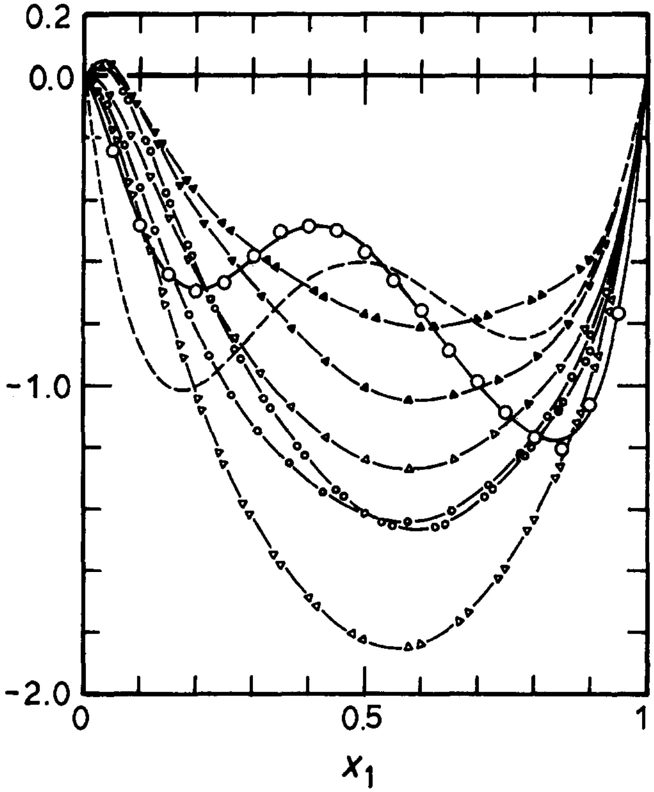

Fig. 3. Excess heat capacity of x polyether + $(1-x)$ *n*-octane or *n*-heptane: ○, 2,5,8-trioxanonane + *n*-octane; — — —, 2,5,8-trioxanonane + *n*-heptane [7]; o, 2,5-dioxanonane + *n*-octane; △, 2,6-dioxanonane + *n*-octane; ▲, 2,7-dioxanonane + *n*-octane; ▲▲, 2,8-dioxanonane + *n*-octane; △△, 3,6-dioxanonane + *n*-octane; oo, 3,7-dioxanonane + *n*-octane.

On the other hand, the V^E for the 2,5,8-trioxanonane + *n*-heptane mixture reported by Treszczanowicz et al. [9] is about 0.95 $\mathrm{cm^{-1}}$ $\mathrm{mol^{-1}}$, and smaller than that of the *n*-octane mixture, probably because of the smaller difference between the molar volumes of the component liquids than that in the latter instance.

The excess heat capacity C_p^E of the 2,5,8-trioxanonane + *n*-octane mixture is negative and is an anomalous W-shaped curve, in line with an effect of non-randomness such as that suggested by Saint-Victor and Patterson [10] Benson and co-workers reported a behavior similar to that of the 2,5,8-trioxanonane + *n*-heptane mixture [7]. The C_p^E curves of the diether mixtures are not W-shaped and not parabolic. They are negative as a whole and seem to increase to a level in the neighbourhood of a minimum of the curve and then flatten out, as described in previous work [1]. This positive contribution becomes more dominant and thus the curve is W-shaped for the triether mixture, as seen in Fig. 3.

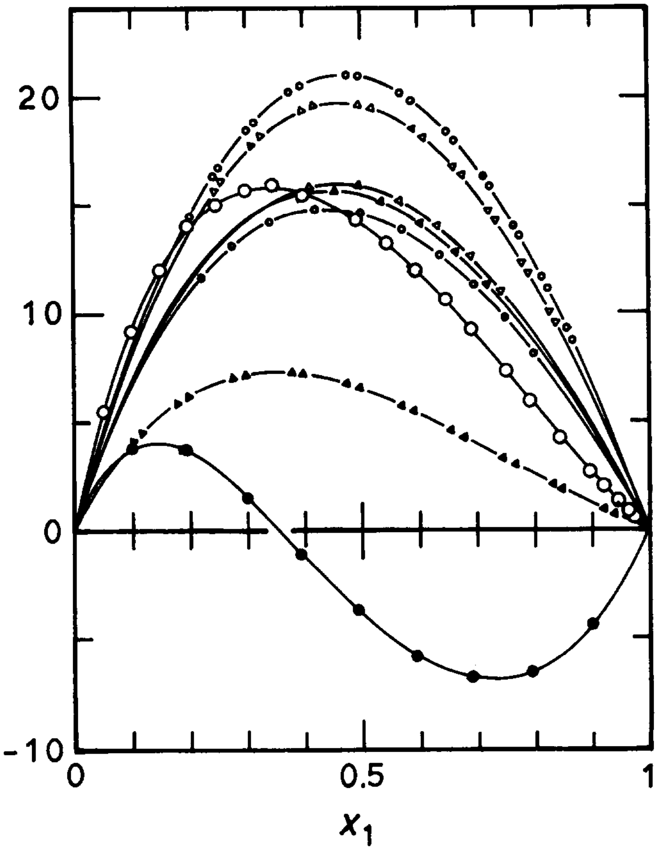

Fig. 4. Excess isentropic compressibility of x polyether + $(1-x)$ n-octane or n-heptane: ○, 2,5,8-trioxanonane + n-octane; ●, 2,5,8-trioxanonane + n-heptane; o, 2,5-dioxanonane + n-octane; △, 2,6-dioxanonane + n-octane; ▲, 2,7-dioxanonane + n-octane; ▲▲, 2,8-dioxanonane + n-octane; △△, 3,6-dioxanonane + n-octane; oo, 3,7-dioxanonane + n-octane.

The excess isentropic compressibility κ_S^E in Fig. 4 and the excess isothermal compressibility κ_T^E in Fig. 5 for the 2,5,8-trioxanonane + n-octane mixture are positive as a whole. The κ_S^E and κ_T^E curves of the diether mixtures are parabolic, except for the 2,8-dioxanonane system [2]. Those for the 2,8-dioxanonane and 2,5,8-trioxanonane mixtures are depressed to a level from the parabolic one in the region of the ether-rich concentration. Non-randomness effects can be found in both the excess compressibilities, as in the excess heat capacities of the latter mixtures, but they are very weak in comparison with those for the 2,5,8-trioxanonane + n-heptane mixture found by Benson and co-workers [9]. The excess compressibility of the triether + n-heptane mixture shows an S-shaped curve; in the case of the 2,5,8-trioxanonane + n-octane mixture the S-shaped curve is displaced to the positive side, because of the larger excess volume in the octane mixture than in the heptane one.

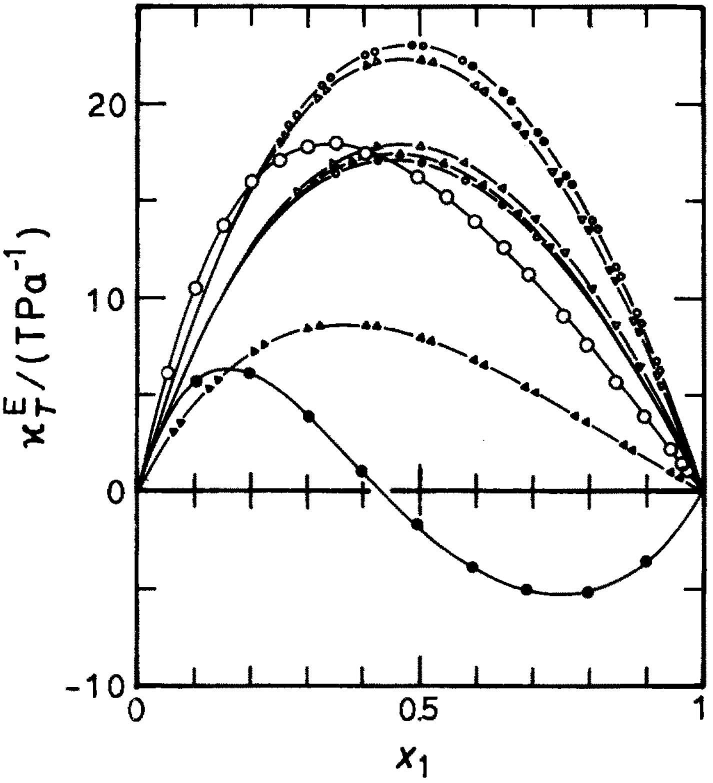

Fig. 5. Excess isothermal compressibility of x polyether + $(1-x)$ *n*-octane or *n*-heptane: ○, 2,5,8-trioxanonane + *n*-octane; ●, 2,5,8-trioxanonane + *n*-heptane; o, 2,5-dioxanonane + *n*-octane; △, 2,6-dioxanonane + *n*-octane; ▲, 2,7-dioxanonane + *n*-octane; ▲▲, 2,8-dioxanonane + *n*-octane; △△, 3,6-dioxanonane + *n*-octane; oo, 3,7-dioxanonane + *n*-octane.

In the triether mixtures there seem to exist two states in admixture; one is a less compressible triether-rich region, owing to the formation of a structure by alignment of dipoles, the other is a more compressible triether-poor region, in which dipolar molecules disperse in the non-polar liquid and change the conformations of any expanded and dipole-aligned structures by intramolecular dipole–dipole interaction, instead of losing intermolecular order. The expanded structure may contribute to the positive part of the excess heat capacity appearing at low concentrations of diethers. In the region of intermediate concentration, the interchange of two states in relation to temperature may rise to the level in the excess heat capacity curve.

In the diether mixtures the above two distinct states cannot be found as clearly as for the triether mixtures, but a considerable local concentration difference or fluctuation may exist, as inferred from the behavior of their excess heat capacities.

CONCLUSIONS

It is concluded from the behaviors of C_p^E and κ_T^E that the triether + *n*-alkane mixture clearly has a large fluctuation or difference of local concentration; in the diether + *n*-alkane mixture the possibility of considerable fluctuation is also suggested.

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