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Thermodynamic properties of mixtures containing 1,3-diphenyl-propane at 298.15 K

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Abstract

Excess enthalpies, excess isobaric heat capacities, densities and speeds of sound of the mixtures, 1,3-diphenylpropane + benzene, + toluene, and + cyclohexane, were measured at 298.15 K. For comparison, the excess isobaric heat capacity of the mixture toluene + cyclohexane was also measured at 298.15 K. The excess volumes were estimated from the density, and the isentropic and isothermal compressibilities and isochoric heat capacities were estimated from density, speed of sound and isobaric heat capacity. The excess enthalpies of all the systems are positive, and that of the mixture of 1,3-diphenylpropane + toluene is nearly zero. All properties of the mixture of 1,3-diphenylpropane and toluene show that 1,3-diphenylpropane can be considered as a dimer of toluene.

Keywords: Excess thermodynamic properties; 1,3-Diphenylpropane; Benzene; Toluene; Cyclohexane

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1. Introduction

To clarify interactions of non-polar molecules in the liquid state, we have studied the physical properties of non-polar binary liquid systems, concentrating on the two effects of the size and aromaticity of the molecules. For this purpose, we measured excess enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$, excess isobaric heat capacities $C_{p,\mathrm{m}}^{\mathrm{E}}$, densities ρ, and speeds of sound u at 298.15 K for the mixtures of 1,3-diphenylpropane

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(DPhP) + benzene, + toluene, and + cyclohexane. From these results, excess volumes V_m^E, excess isentropic compressibilities κ_S^E, excess isothermal compressibilities κ_T^E, and excess isochoric heat capacitis $C_{V,m}^E$ for these systems are calculated. The $C_{p,m}^E$ value for the mixture of toluene + cyclohexane was measured to discuss the effect of molecular size.

2. Experimental

Benzene, toluene, and cyclohexane, all special grade reagents from Wako Pure Chemical Industry Ltd., were fractionally distilled at atmospheric pressure to exceed 99.95% purity (GlC and moisture detection). 1,3-Diphenylpropane obtained by Wolff–Kishner reduction of dibenzylketone was purified by fractional distillation at a reduced pressure of about 1 mm Hg. The purity was above 99.8% (GlC).

Excess enthalpies were measured with an LKB microcalorimeter (LKB 107001); isobaric heat capacities of the pure components and excess values of the mixtures were measured with a home-made flow microcalorimeter; densities with a vibrating-tube densimeter (Anton Paar, DMA602); and speeds of sound by a sing-around method (Cho-onpa Ind., UVM-2). All the values reported here are of the properties at 298.15 K. Details of the measurements are found in previous papers [1–4].

The accuracies of the excess enthalpy, excess isobaric heat capacity, density, and speed of sound measurements are ±0.2%, $\pm 0.01\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $\pm 0.00001\ \mathrm{g\,cm^{-1}}$, and $\pm 0.3\ \mathrm{m\,s^{-1}}$, respectively.

Details of the estimations of excess isentropic and isothermal compressibilities and the isochoric heat capacity are described elsewhere [3].

Table 1
Physical properties of materials used at 298.15 K

Property	1,3-Diphenylpropane	Benzene	Toluene	Cyclohexane
$\rho/\mathrm{g\,cm^{-3}}$	0.97577	0.87362	0.86221	0.77384
$u/\mathrm{m\,s^{-1}}$	1508.6	1299.6	1305.3	1254.4
$C_{p,m}/\mathrm{J\,K^{-1}\,mol^{-1}}$	326.9	135.76	157.29	156.01
$10^3\alpha/\mathrm{K^{-1}}$	0.774[a]	1.218[b]	1.09[c]	1.216[b]
$\kappa_S/\mathrm{TPa^{-1}}$	450.30	677.73	680.72	821.25
$\kappa_T/\mathrm{TPa^{-1}}$	560.2	969.0	921.4	1128.6
$C_{V,m}/\mathrm{J\,K^{-1}\,mol^{-1}}$	262.7	95.0	116.2	113.6

[a] From densities at 298.15 and 303.15 K.
[b] From Ref. [4].
[c] From Ref. [5].

Table 2
Excess enthalpies of the mixtures at 298.15 K

x	$H^{\mathrm{E}}_{\mathrm{m}}$ J mol^{-1}	x	$H^{\mathrm{E}}_{\mathrm{m}}$ J mol^{-1}
$x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$			
0.02500	138.9	0.55000	880.5
0.05000	264.9	0.60000	844.4
0.10000	473.3	0.65000	781.8
0.15000	625.2	0.70000	716.4
0.20000	750.3	0.75000	635.2
0.25000	826.6	0.80000	541.2
0.30000	881.4	0.85000	432.6
0.35000	915.1	0.90000	268.6
0.40000	920.0	0.95000	155.3
0.45000	927.0	0.97500	84.1
0.50000	905.4		
$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$			
0.02500	4.73	0.55000	48.84
0.05000	9.64	0.60000	46.63
0.10000	18.93	0.65000	43.32
0.15000	27.28	0.70000	39.37
0.20100	34.92	0.75000	34.71
0.25000	40.58	0.80000	29.43
0.30000	44.91	0.85000	23.08
0.35000	47.77	0.90000	15.83
0.40000	49.76	0.95000	8.60
0.45000	50.37	0.97500	4.17
0.50000	50.11		
$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$			
0.02499	−0.10	0.54991	7.53
0.04998	0.36	0.59991	7.29
0.09997	1.03	0.64992	6.71
0.14996	2.18	0.69993	5.83
0.19994	3.81	0.74993	5.40
0.24993	4.81	0.80000	4.72
0.29993	5.63	0.84995	3.17
0.34992	6.30	0.89997	2.13
0.39991	6.74	0.94998	0.81
0.44991	7.09	0.97499	0.15
0.49991	7.61		

3. Results and discussion

The physical properties of the components are given in Table 1. The values of $H^{\mathrm{E}}_{\mathrm{m}}$ for the mixtures of DPhP + benzene, DPhP + toluene, and DPhP + cyclohexane are given in Table 2. The $C^{\mathrm{E}}_{p,\mathrm{m}}$ values for these systems are given in Table 3. The $V^{\mathrm{E}}_{\mathrm{m}}$, κ^{E}_{S}, κ^{E}_{T},

Table 3
Excess isobaric heat capacities of the mixtures at 298.15 K

x	$C^{E}_{p,m}$ J K^{-1} mol^{-1}	x	$C^{E}_{p,m}$ J K^{-1} mol^{-1}
$x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$			
0.02499	−0.48	0.49994	−3.89
0.04999	−0.97	0.54994	−3.86
0.09998	−1.89	0.59994	−3.66
0.14997	−2.51	0.64995	−3.50
0.19997	−2.96	0.69995	−2.92
0.24996	−3.34	0.74996	−2.78
0.29995	−3.63	0.79996	−2.35
0.34995	−3.81	0.84997	−2.13
0.39995	−3.96	0.94999	−1.01
0.44994	−3.94	0.97500	−0.49
$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$			
0.02499	−0.12	0.54993	−1.66
0.04999	−0.30	0.59992	−1.65
0.09997	−0.63	0.64993	−1.46
0.14996	−0.82	0.69994	−1.51
0.19995	−1.02	0.74994	−1.32
0.24994	−1.22	0.79995	−1.21
0.29994	−1.38	0.84996	−1.01
0.34993	−1.48	0.89997	−0.81
0.39993	−1.61	0.94999	−0.48
0.44993	−1.65	0.97499	−0.23
0.49993	−1.65		
$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$			
0.02500	−0.05	0.54998	−1.42
0.05000	−0.14	0.59998	−1.41
0.10000	−0.38	0.64999	−1.37
0.15000	−0.55	0.69999	−1.31
0.19999	−0.70	0.74999	−1.29
0.24888	−0.85	0.79999	−1.18
0.29999	−1.02	0.84999	−1.00
0.34998	−1.13	0.89999	−0.80
0.39998	−1.23	0.95000	−0.46
0.44998	−1.32	0.97500	−0.24
0.49998	−1.38		
$x(C_6H_5CH_3 + (1-x)c\text{-}C_6H_{12}$			
0.02500	−0.21	0.54998	−1.90
0.05000	−0.37	0.59998	−1.87
0.09999	−0.75	0.64998	−1.77
0.14999	−1.08	0.69999	−1.64
0.19999	−1.27	0.74999	−1.50
0.24999	−1.52	0.79999	−1.31

Table 3 *(continued)*

x	$C^{\mathrm{E}}_{p,\mathrm{m}}$ J K^{-1} mol^{-1}	x	$C^{\mathrm{E}}_{p,\mathrm{m}}$ J K^{-1} mol^{-1}
0.29999	−1.66	0.84999	−1.07
0.34998	−1.78	0.89999	−0.75
0.39998	−1.87	0.95000	−0.40
0.44999	−1.92	0.97500	−0.23
0.49998	−1.92		

Table 4
Excess volumes, excess isentropic and isothermal compressibilities and excess isochoric heat capacities at 298.15 K

x	$V^{\mathrm{E}}_{\mathrm{m}}$ cm^3 mol^{-1}	κ^{E}_S TPa^{-1}	κ^{E}_T TPa^{-1}	$C^{\mathrm{E}}_{V,\mathrm{m}}$ J K^{-1} mol^{-1}
		$x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$		
0.02518	0.022	−5.31	−4.2	−0.74
0.05008	0.101	−9.21	−7.1	−1.38
0.09994	0.170	−17.20	−13.3	−2.50
0.14976	0.221	−22.07	−18.2	−3.39
0.19985	0.252	−26.15	−22.0	−4.14
0.24969	0.268	−29.05	−24.9	−4.75
0.30034	0.282	−30.67	−26.6	−5.24
0.34842	0.288	−31.51	−27.4	−5.59
0.40075	0.285	−31.21	−27.6	−5.83
0.45306	0.283	−30.49	−27.2	−5.93
0.50452	0.265	−28.99	−26.0	−5.89
0.54997	0.243	−27.41	−24.7	−5.75
0.59525	0.221	−25.55	−23.2	−5.53
0.65175	0.202	−22.61	−20.6	−5.14
0.69899	0.175	−20.02	−18.3	−4.74
0.75048	0.153	−16.89	−15.5	−4.24
0.80198	0.121	−13.67	−12.5	−3.67
0.85138	0.088	−10.44	−9.6	−3.05
0.90081	0.063	−7.03	−6.4	−2.28
0.95033	0.024	−3.66	−3.3	−1.32
0.97692	0.017	−1.68	−1.5	−0.67
		$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$		
0.02221	−0.025	−3.76	−3.6	−0.27
0.05170	−0.051	−8.03	−7.6	−0.63
0.10022	−0.086	−13.32	−12.6	−1.16
0.15184	−0.112	−17.12	−16.2	−1.62
0.20588	−0.133	−19.35	−18.3	−2.06
0.24881	−0.145	−20.37	−19.3	−2.33
0.32378	−0.151	−21.01	−19.9	−2.69
0.40062	−0.151	−20.38	−19.3	−2.90
0.42812	−0.151	−19.82	−18.8	−2.93

Table 4 *(continued)*

x	V_m^E $cm^3 mol^{-1}$	κ_S^E TPa^{-1}	κ_T^E TPa^{-1}	$C_{V,m}^E$ $J K^{-1} mol^{-1}$
0.47501	−0.147	−18.73	−17.7	−2.94
0.56623	−0.131	−16.09	−15.2	−2.85
0.57278	−0.128	−15.87	−15.0	−2.83
0.61403	−0.122	−14.44	−13.7	−2.73
0.62643	−0.118	−14.03	−13.3	−2.70
0.70934	−0.100	−11.07	−10.4	−2.39
0.78360	−0.074	−8.26	−7.8	−2.01
0.79636	−0.074	−7.88	−7.4	−1.94
0.83600	−0.059	−6.25	−5.9	−1.66
0.86414	−0.050	−5.18	−4.8	−1.45
0.94146	−0.020	−2.31	−1.6	−0.73
0.96701	−0.014	−1.28	−1.2	−0.43
0.97064	−0.009	−1.12	−1.0	−0.39
$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6CH_3$				
0.02376	−0.024	−3.91	−3.8	−0.27
0.04927	−0.073	−7.44	−7.3	−0.54
0.10400	−0.136	−13.39	−13.1	−1.09
0.15035	−0.176	−16.99	−16.5	−1.50
0.18931	−0.200	−19.32	−18.8	−1.82
0.24239	−0.228	−21.13	−20.5	−2.16
0.28768	−0.246	−21.83	−21.2	−2.38
0.34307	−0.260	−22.12	−21.5	−2.59
0.39445	−0.266	−21.88	−21.2	−2.71
0.43265	−0.264	−21.20	−20.6	−2.74
0.49894	−0.251	−19.69	−19.1	−2.73
0.54106	−0.243	−18.51	−18.0	−2.68
0.59821	−0.227	−16.66	−16.2	−2.54
0.62019	−0.221	−15.87	−15.4	−2.47
0.70087	−0.188	−12.89	−12.5	−2.16
0.74071	−0.166	−11.22	−10.9	−1.97
0.79850	−0.131	−8.84	−8.6	−1.65
0.84623	−0.104	−6.75	−6.5	−1.33
0.89567	−0.075	−4.63	−4.5	−0.97
0.94827	−0.037	−2.33	−2.3	−0.52

and $C_{V,m}^E$ values are estimated from the density, speed of sound and isobaric heat capacity of the mixture and are shown in Table 4.

The excess values are plotted against mole fraction of DPhP in Figs. 1–5, together with the curves expressed by the Redlich–Kister equation

$$F^E = x(1-x)[1-G(1-2x)]^{-1} \sum A_i(1-2x)^{i-1} \qquad (1)$$

where A_i are parameters estimated by the least-squares method with iterative G and given in Table 5.

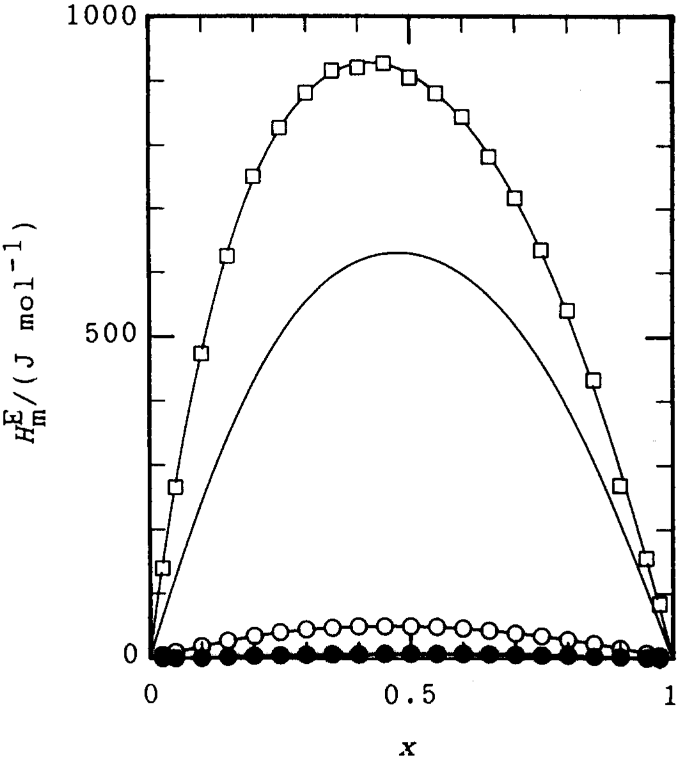

Fig. 1. Excess enthalpies of the mixtures at 298.15 K: ○, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$; ●, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$; □, $x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$; —, $xC_6H_5CH_3 + (1-x)c\text{-}C_6H_{12}$.

For all systems, the H^{E}_{m} values are positive over the whole range of concentration, as seen in Fig. 1. Those of the mixtures of DPhP + benzene and DPhP + toluene are much smaller than those of the mixture of DPhP + cyclohexane. The H^{E}_{m} value of the first mixture is very similar to that of the mixture of toluene and benzene [6]. The breaking of aromatic–aromatic interactions between the like molecules is recovered by the formation of aromatic–aromatic interactions between the unlike molecules. The H^{E}_{m} value of the third mixture also corresponds to that of the mixture of toluene and cyclohexane [7], considering DPhP as a dimer of toluene. Aromatic–aromatic interactions are broken by mixing and show large endotherms. H^{E}_{m} is determined by the constituents of the component molecules. The order of the H^{E}_{m} values corresponds to the differences in the ratio of the aromatic part to the whole molecule. In this respect, DPhP is similar to toluene, not so different from benzene, but different from cyclohexane. In Fig. 2, this tendency is also found in the $C^{E}_{p,m}$ values which are negative, and follow the same order as the positivities of H^{E}_{m}, confirming that molecules interact more favorably with like molecules than with unlike ones. The differences among the

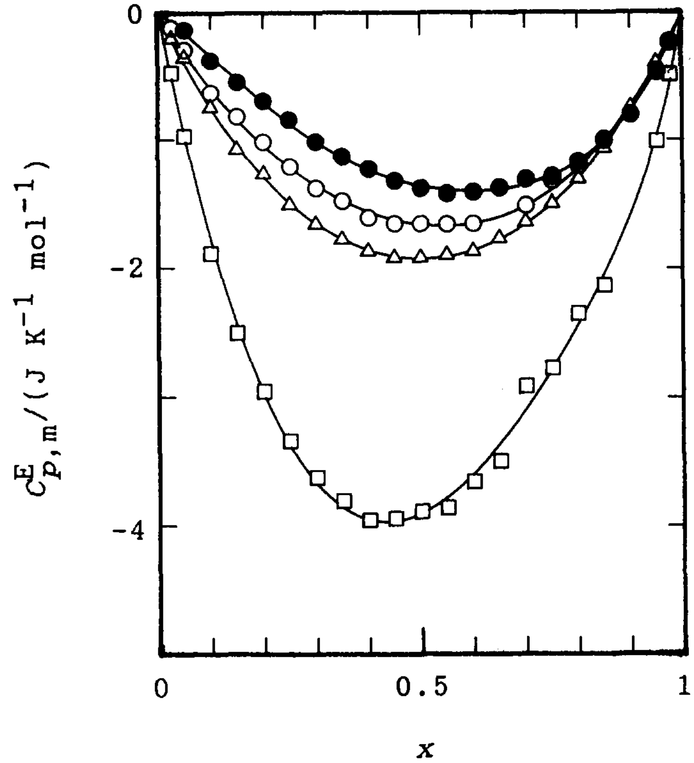

Fig. 2. Excess isobaric heat capacities of the mixtures at 298.15 K: ○, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$; ●, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$; □, $x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$; △, $xC_6H_5CH_3 + (1-x)c\text{-}C_6H_{12}$.

$C^E_{p,m}$ values of these three systems are not so remarkable as among the H^E_m values. It has to be noted that the sign of H^E_m for the mixture of DPhP + toluene is expected to change from positive to negative with an increase in temperature of ten degrees, in consideration of H^E_m and $C^E_{p,m}$ at 298.15 K in this system.

V^E_m depends on the difference in molecular sizes as well as on energetical considerations. In Fig. 3, the values of V^E_m for the mixture of DPhP + cyclohexane are positive, as expected from the positive H^E_m; this is attributed to the difference between the constituents of the two components. They are less than the values of the toluene + cyclohexane mixture [6], owing to the difference in the molecular sizes of the components. However, V^E_m values for the mixtures of DPhP + benzene and DPhP + toluene are negative, contrary to expectation from H^E_m. This may be ascribed to the difference in molecular sizes. When two components of different sizes are mixed, the free volume found in the pure state of the larger molecule, in the present case DPhP, will be occupied by the smaller molecule. Consequently the molecules are more closely packed and volumes of the solutions are reduced. This situation does not occur in the

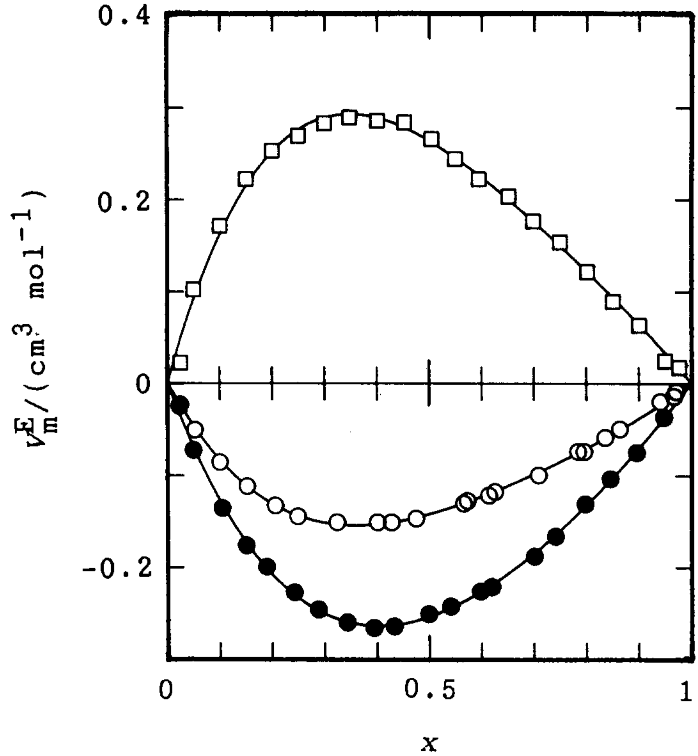

Fig. 3. Excess volumes of the mixtures at 298.15 K: ○, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$; ●, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$; □, $x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$.

mixtures of toluene + benzene [8] and toluene + cyclohexane [6], where the molecular sizes are similar. The positive V_m^E for the mixture of toluene + benzene is also reduced to a negative value for the mixture of DPhP + benzene, as is the case in cyclohexane mixtures.

More information on the local arrangement of the molecules is obtained from κ_T^E. The κ_T^E and κ_S^E values are negative sign for all the systems, as illustrated in Figs. 4 and 5. This suggests that molecules are confined to a specified region around the DPhP. DPhP has two types of regions around itself: one prefers aromatic or unsaturated hydrocarbons which reduces the volume of the solution; the other prefers and attracts saturated hydrocarbons, which enlarges the volume, because of unfavorable occupations of the major aromatic site of DPhP by the aliphatic molecules. The negative κ_T^E of the DPhP + cyclohexane mixture, together with its positive V_m^E, informs us that cyclohexane breaks the aromatic–aromatic interaction of DPhP and the conformation of DPhP is so restricted that cyclohexane is confined to the small aliphatic region around DPhP and leaves the rest of the space

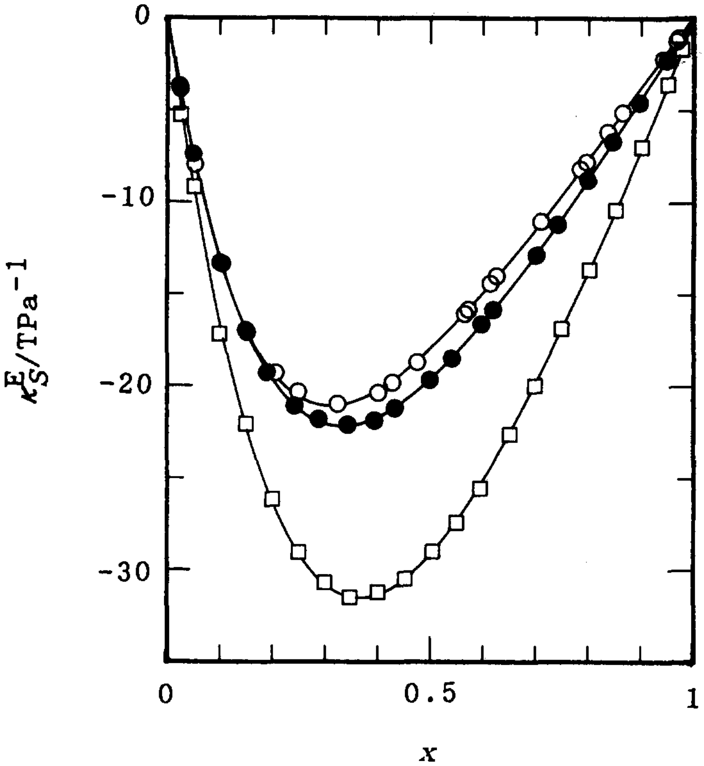

Fig. 4. Excess isentropic compressibilities of the mixtures at 298.15 K: ○, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$; ●, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$; □, $x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$.

free for aromatics. The aromatic–aromatic interaction forms a stiff network. The negative κ_T^E value confirms that the smaller molecule is restricted to a like-site of DPhP, whichever type it is.

Negative κ_T^E and κ_S^E values suggest that molecules are localized at a favorable site of DPhP, that stable aromatic–aromatic interaction is dominant in any system, and that the interaction is considerably stiff.

$C_{V,m}^E$ is of the order of $C_{p,m}^E$ and seems to be more negative. We cannot, however, comment any further on this because of neglecting the excess expansion coefficient α^E on estimation of $C_{V,m}$ and κ_T. However, α^E may be less than $10^{-5}\,K^{-1}$ as usual in non-polar mixtures and then the effect of α^E can be negligible. These system may correspond to such a case.

As a result, the DPhP molecule is a toluene-like molecule and can be regarded as a dimer of toluene for cyclohexane, benzene, and toluene.

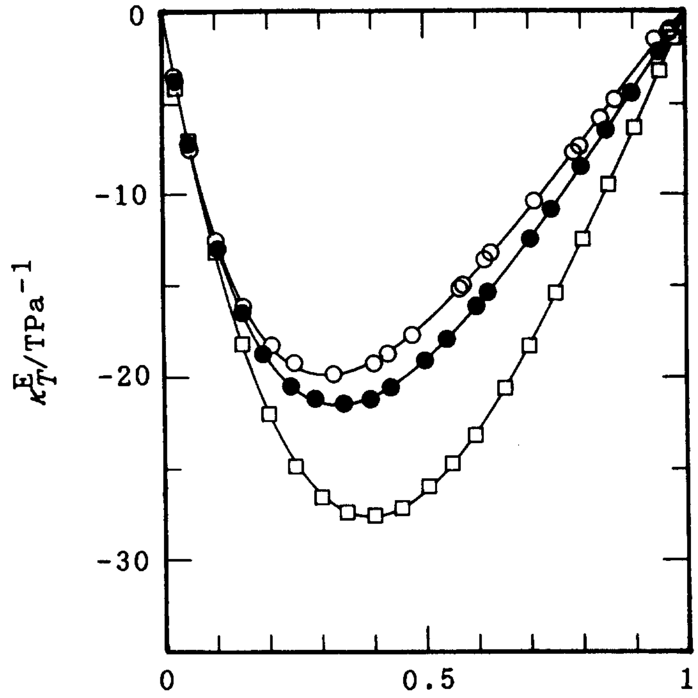

Fig. 5. Excess isothermal compressibilities of the mixtures at 298.15 K: ○, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$; ●, $x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_5CH_3$; □, $x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$.

Table 5
Parameters of Eq. (1) and standard deviations s of the properties of the mixtures at 298.15 K

Property	A_1	A_2	A_3	A_4	G	s
			$x(C_6H_5CH_2)_2CH_2 + (1-x)c\text{-}C_6H_{12}$			
$H_m^E/J\,mol^{-1}$	3642.4	871.6	975.5	602.7		7.9
$C_{p,m}^E/J\,K^{-1}\,mol^{-1}$	−15.62	−16.43	−5.90		−0.80441	0.08
$V_m^E/cm^3\,mol^{-1}$	1.051	0.675	0.310			0.008
κ_S^E/TPa^{-1}	−116.71	−65.04	−24.61			0.20
κ_T^E/TPa^{-1}	−105.0	−48.8	−8.9			0.1
$C_{V,m}^E/J\,K^{-1},mol^{-1}$	−23.46	−22.78	−5.26		−0.82463	0.03
			$x(C_6H_5CH_2)_2CH_2 + (1-x)C_6H_6$			
$H_m^E/J\,mol^{-1}$	201.14	36.25	−6.96	−24.88		0.26
$C_{p,m}^E/J\,K^{-1}\,mol^{-1}$	−6.65	0.92	−1.26			0.04
$V_m^E/cm^3\,mol^{-1}$	−0.570	−0.314	−0.173			0.002
κ_S^E/TPa^{-1}	−71.98	−54.41	−34.62	−16.92		0.11
κ_T^E/TPa^{-1}	−68.2	−50.7	−30.8	−20.0		0.1
$C_{V,m}^E/J\,K^{-1}\,mol^{-1}$	−11.71	−0.58	−1.56			0.03

Table 5 *(continued)*

Property	A_1	A_2	A_3	A_4	G	s
			$x(C_6H_5CH_2)_2CH_2+(1-x)C_6H_5CH_3$			
$H_m^E/J\,mol^{-1}$	30.25	−4.32	−17.07			0.26
$C_{p,m}^E/J\,K^{-1}\,mol^{-1}$	−5.45	1.61	−1.22	2.15		0.02
$V_m^E/cm^3\,mol^{-1}$	−1.016	−0.392	−0.139			0.004
κ_S^E/TPa^{-1}	−78.64	−52.75	−28.75	−11.34		0.06
κ_T^E/TPa^{-1}	−76.3	−50.9	−28.1	−12.6		0.1
$C_{V,m}^E/J\,K^{-1}\,mol^{-1}$	−10.92	−1.36	−0.18			0.02
			$xC_6H_5CH_3+(1-x)c\text{-}C_6H_{12}$			
$C_{p,m}^E/J\,K^{-1}\,mol^{-1}$	−7.72	0.01	−1.08			0.02

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