Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 2, 587–595

ENTHALPIES OF MIXING OF *o*- AND *m*-ISOMERS AT 298.15 K

T. Kimura[*], *Y. Takahashi, T. Kamiyama and M. Fujisawa*

Department of Chemistry, Kinki University, 3-4-1 Kowakae, Higashi-osaka 577-8502, Japan

Excess enthalpies (H^E) of 17 binary mixtures of *o*- and *m*-isomers of dichlorobenzene, difluorobenzene, methoxymethylbenzene, dimethylbenzene, dimethoxybenzene, aminofluorobenzene, fluoronitrobenzene, diethylbenzene, chlorofluorobenzene, fluoroiodobenzene, bromofluorobenzene, chloromethylbenzene, fluoromethylbenzene, bromomethylbenzene, iodomethylbenzene, fluoromethoxybenzene, dibromobenzene at 298.15 K were measured. All excess enthalpies measured were very small, and those of *o*-+*m*-isomers of aminofluorobenzene, dibromobenzene and iodomethylbenzene were negative but 14 other binary mixtures of isomers were positive over the whole range of mole fractions. H^E of *o*-+*m*-isomers of dimethoxybenzene showed the largest enthalpic instability and those of aminofluorobenzene showed the largest enthalpic stability. There was a correlation between dipole–dipole interaction, dipole–induced dipole interaction or entropies of vaporization and excess partial molar enthalpies at infinite dilution.

Keywords: *dipole–dipole interaction, dipole–induced dipole interaction, entropy of vaporization, excess enthalpy, o-, m-isomer structural isomer*

Introduction

It is important to show how the molecules that constitute a solution in a liquid state recognize themselves mutually for understanding various reactions. Most of interactions of optical isomers are unclear, structural and isotopic isomerisms have the same kind and number of functional groups in a molecule. It is important to clarify the thermodynamic property of a solution by the slight differences in the structures of molecules. In order to understand the origin of the isotope effect on intermolecular interactions and the excess thermodynamic functions of binary mixtures of simple molecules under ambient conditions compared with theoretical treatment [1], excess enthalpies of binary mixtures of isotopic systems have been reported [2, 3]. Also some binary systems of enantiomers and solutions of enantiomers have been reported and their mutual interactions discussed [4–13].

From the viewpoint of the mutual interaction of isomers, Benson *et al.* [14, 15] reported excess enthalpies of *o*-, *m*-, *p*-isomer of dimethylbenzene. In order to obtain further systematic information for the effect on the intermolecular interaction of the structural isomerism in liquid-state, the excess enthalpies of 17 binary mixtures of *o*- and *m*-isomers were determined at 298.15 K.

Experimental

o- and *m*-isomers of dichlorobenzene, difluorobenzene, methoxymethylbenzene, dimethylbenzene, dimethoxybenzene, aminofluorobenzene, fluoronitrobenzene, diethylbenzene, chlorofluorobenzene, fluoroiodobenzene, bromofluorobenzene, chloromethylbenzene, fluoromethylbenzene, bromomethylbenzene, iodomethylbenzene, fluoromethoxybenzene, dibromobenzene (Kishida Chemical, for spectrum) were fractionally distilled over freshly activated molecular sieves 4 Å that had been evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa. The results of purity analyses with the gas–liquid chromatograms obtained by using 2 m columns of 10% SE-30 on WAW chromosorb and 20% PEG-1000 on celite 545 with FID on Yanagimoto model G180FP were more than 99.9 mol%. Water contents with the coulometric Karl–Fischer's method on a Mitsubishi Moisture Meter model CA-02 (Mitsubishi Chemical Ind.) were less than 0.002 mol%. Densities of the samples measured by a vibrating-tube densitometer (Anton Paar D60) at 298.15±0.001 K are listed in the fourth column of Table 1. The details of the densimetric procedures are the same as those described elsewhere [16].

A twin-microcalorimeter of heat-conduction type, Thermal Activity Monitor (Thermometric AB, Järfälla, Sweden) with a mixing vessel of 0.8 cm^3,

---

[*] Author for correspondence: kimura@chem.kindai.ac.jp

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Measured densities and physicochemical properties of *o*- and *m*-isomers at 298.15 K

Samples	ρ(obs.)/g cm^{-3}	$10^{30}\mu^{\mathrm{B}}$/cm	$10^{3\circ}\alpha^{\mathrm{B}}$/m^{3}	ΔS_{vap}/J K^{-1} mol^{-1}
o-dimethylbenzene	0.87594	1.57	14.10	86.48$^{\mathrm{A}}$
m-dimethylbenzene	0.86011	1.02	14.10	86.19$^{\mathrm{A}}$
o-diethylbenzene	0.87612	1.30	17.77	88.14$^{\mathrm{B}}$
m-diethylbenzene	0.85969	1.00	17.18	88.12$^{\mathrm{B}}$
o-dimethoxybenzene	1.0799	3.69	15.40	88.52$^{\mathrm{A}}$
m-dimethoxybenzene	1.0632	7.07	15.40	88.74$^{\mathrm{B}}$
o-difluorobenzene	1.1629	9.01	10.30	87.90$^{\mathrm{B}}$
m-difluorobenzene	1.1510	5.21	10.30	87.10$^{\mathrm{B}}$
o-dichlorobenzene	1.3003	6.62	14.30	88.11$^{\mathrm{A}}$
m-dichlorobenzene	1.2828	4.14	14.30	88.10$^{\mathrm{A}}$
o-dibromobenzene	1.9715	7.21	15.69	88.90$^{\mathrm{B}}$
m-dibromobenzene	1.9473	4.56	15.69	88.74$^{\mathrm{B}}$
o-fluoronitrobenzene	1.3291	19.61	12.06	88.94$^{\mathrm{B}}$
m-fluoronitrobenzene	1.3160	15.05	12.06	88.42$^{\mathrm{B}}$
o-fluoromethoxybenzene	1.1240	3.81	14.20	87.67$^{\mathrm{A}}$
m-fluoromethoxybenzene	1.1077	4.93	14.20	87.77$^{\mathrm{A}}$
o-aminofluorobenzene	1.1476	6.20	11.69	91.89$^{\mathrm{B}}$
m-aminofluorobenzene	1.1510	8.44	11.69	91.96$^{\mathrm{B}}$
o-fluoromethylbenzene	0.99853	6.33	12.82	87.28$^{\mathrm{B}}$
m-fluoromethylbenzene	0.99195	3.20	12.82	87.29$^{\mathrm{B}}$
o-chloromethylbenzene	1.0775	4.65	12.18	87.74$^{\mathrm{A}}$
m-chloromethylbenzene	1.0672	5.81	12.18	87.79$^{\mathrm{A}}$
o-bromomethylbenzene	1.4178	4.31	14.90	88.09$^{\mathrm{B}}$
m-bromomethylbenzene	1.3990	5.37	14.90	88.13$^{\mathrm{B}}$
o-iodomethylbenzene	1.7176	4.32	17.30	88.62$^{\mathrm{B}}$
m-iodomethylbenzene	1.6975	5.30	17.30	88.64$^{\mathrm{B}}$
o-methoxymethylbenzene	0.97434	4.37	14.70	87.97$^{\mathrm{B}}$
m-methoxymethylbenzene	0.96639	3.39	14.70	87.98$^{\mathrm{B}}$
o-chlorofluorobenzene	1.2346	7.66	12.30	87.50$^{\mathrm{B}}$
m-chlorofluorobenzene	1.2206	4.78	12.30	87.40$^{\mathrm{B}}$
o-bromofluorobenzene	1.6046	8.03	13.00	87.75$^{\mathrm{B}}$
m-bromofluorobenzene	1.5862	4.93	13.00	87.65$^{\mathrm{B}}$
o-fluoroiodobenzene	1.9206	7.91	15.40	88.25$^{\mathrm{B}}$
m-fluoroiodobenzene	1.9033	4.88	15.40	88.68$^{\mathrm{B}}$

μ – dipole moment; α – polarizability: $^{\mathrm{A}}$cited values from [16]; $^{\mathrm{B}}$calculated values from quantum chemical method [13–15]

which was modified by the present authors, and the details of the procedures are the same as those described elsewhere [17]. In order to determine the precision of the calorimeter for small enthalpy change, excess enthalpies of 1,4-dimethylbenzene+1,3-dimethylbenzene and *p*-dimethylbenzene+*o*-dimethylbenzene at 298.15 K were measured by three different principle calorimeters. Previous work [3] showed that the results by four different principle calorimeters agreed well.

Results and discussion

The measured densities of the *o*- and *m*-isomer are shown in Table 1. The excess enthalpies of 17 binary mixtures of *o*- and *m*-isomers are given in Table 2 shown in Fig. 1. The values fit Eq. (1) by the method of least squares.

$$H^{E}/\mathrm{J\ mol^{-1}} = (1-x)x\sum_{\mathrm{i}=1}^{\mathrm{k}} A_{\mathrm{i}}\,(1-2x)^{\mathrm{i}-1} \qquad (1)$$

Table 2 Excess enthalpies of (1–x)o-isomer+xm-isomer 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}
(1–x)o-dimethylbenzene+xm-dimethylbenzene							
0.07597	3.559	0.3652	11.21	0.6854	10.18	0.7315	9.350
0.1412	6.013	0.3967	11.52	0.5203	11.83	0.7841	8.138
0.1978	7.839	0.4252	11.67	0.5345	11.80	0.8449	6.408
0.2474	9.199	0.4511	11.77	0.5766	11.41	0.9159	3.871
0.2913	10.11	0.4889	11.92	0.6088	11.18		
0.3303	10.76	0.5051	11.88	0.6449	10.84		
(1–x)o-diethylbenzene+xm-diethylbenzene							
0.09131	2.180	0.3761	6.616	0.5466	7.051	0.7176	5.730
0.1673	3.580	0.4456	6.954	0.5595	6.998	0.7721	4.942
0.2316	4.874	0.4749	7.053	0.5921	6.887	0.8355	3.880
0.2867	5.637	0.5012	7.095	0.6288	6.683	0.9104	2.350
0.3344	6.338	0.5250	7.070	0.6702	6.3990		
(1–x)o-dimethoxybenzene+xm-dimethoxybenzene							
0.08056	22.80	0.3445	62.38	0.5095	63.91	0.7003	50.11
0.1491	37.97	0.3801	64.35	0.5388	62.83	0.7570	42.79
0.2081	47.95	0.4121	65.36	0.5718	61.20	0.8237	33.01
0.2595	54.76	0.4594	65.09	0.6091	58.73	0.9033	18.98
0.3046	59.44	0.4831	64.77	0.6515	55.07		
(1–x)o-difluorobenzene+xm-difluorobenzene							
0.1201	6.220	0.2206	10.44	0.3578	14.93	0.6202	16.66
0.1268	6.546	0.2317	10.84	0.3880	15.63	0.6621	15.92
0.1344	6.878	0.2440	11.27	0.4237	16.34	0.7101	14.77
0.1428	7.279	0.2577	11.71	0.4711	17.34	0.7656	13.04
0.1525	7.734	0.2729	12.24	0.4949	17.43	0.8305	10.37
0.1635	8.256	0.2902	12.80	0.5213	17.41	0.9074	6.312
0.1762	8.844	0.3097	13.46	0.5505	17.34		
0.2105	10.07	0.3320	14.15	0.5833	17.11		
(1–x)o-dichlorobenzene+xm-dichlorobenzene							
0.07857	1.934	0.4342	8.659	0.5502	9.272	0.8547	5.713
0.1456	3.637	0.4602	8.948	0.5666	9.260	0.9216	3.391
0.2036	4.899	0.4776	9.074	0.5953	9.257		
0.2543	5.958	0.4940	9.151	0.6270	9.228		
0.2989	6.798	0.5093	9.240	0.6623	8.992		
0.3385	7.395	0.5237	9.237	0.7018	8.693		
0.3737	7.921	0.5374	9.257	0.7463	8.094		
0.4055	8.341	0.5406	9.198	0.7968	7.101		
(1–x)o-dibromobenzene+xm-dibromobenzene							
0.08885	–2.746	0.4056	–5.616	0.5607	–4.547	0.7929	–1.946
0.1632	–4.312	0.4382	–5.459	0.5895	–4.300	0.8517	–1.328
0.2263	–5.150	0.4674	–5.235	0.6214	–3.944	0.9199	–0.626
0.2806	–5.577	0.4891	–5.120	0.6569	–3.565		
0.3277	–5.668	0.5109	–4.977	0.6967	–3.108		
0.3691	–5.681	0.5346	–4.787	0.7417	–2.539		

Table 2 Continued

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
(1–x)*o*-fluoromethylbenzene+x*m*-fluoromethylbenzene							
0.1293	1.875	0.2635	3.464	0.4579	4.348	0.7716	2.834
0.1788	2.481	0.2862	3.665	0.4912	4.377	0.8711	1.785
0.1968	2.714	0.3132	3.857	0.5297	4.355		
0.2188	2.949	0.3458	4.029	0.5747	4.222		
0.2275	3.063	0.3859	4.202	0.6282	3.960		
0.2442	3.261	0.4366	4.337	0.6925	3.536		
(1–x)*o*-chloromethylbenzene+x*m*-chloromethylbenzene							
0.0907	2.163	0.3744	6.414	0.5323	6.429	0.7192	5.105
0.1663	3.752	0.4111	6.538	0.5615	6.356	0.7735	4.471
0.2303	4.807	0.4438	6.582	0.5940	6.189	0.8366	3.590
0.2851	5.643	0.4730	6.549	0.6306	5.961	0.9110	2.159
0.3327	6.122	0.4993	6.499	0.6720	5.619		
(1–x)*o*-bromomethylbenzene+x*m*-bromomethylbenzene							
0.09232	2.032	0.3084	5.067	0.5179	5.715	0.7632	3.842
0.1690	3.252	0.3405	5.346	0.5472	5.634	0.8286	3.027
0.2240	4.140	0.3800	5.589	0.5800	5.438	0.9062	1.772
0.2405	4.334	0.4462	5.788	0.6170	5.187		
0.2596	4.563	0.4678	5.800	0.6591	4.887		
0.2819	4.790	0.4915	5.783	0.7073	4.473		
(1–x)*o*-iodomethylbenzene+x*m*-iodomethylbenzene							
0.09118	–0.8845	0.4479	–1.986	0.6635	–1.605	0.9079	–0.5470
0.1686	–1.213	0.5035	–1.968	0.7114	–1.388		
0.2885	–1.745	0.5489	–1.873	0.7667	–1.183		
0.3782	–1.945	0.6217	–1.750	0.8313	–0.9104		
(1–x)*o*-methylmethoxybenzene+x*m*-methylmethoxybenzene							
0.08196	1.000	0.2512	2.692	0.4039	3.413	0.5814	3.203
0.1318	1.599	0.2684	2.812	0.4299	3.456	0.6135	3.110
0.1373	1.639	0.2881	2.942	0.4594	3.447	0.6494	2.961
0.1433	1.694	0.3109	3.082	0.4808	3.469	0.6897	2.709
0.2000	2.353	0.3254	3.153	0.4933	3.413	0.7353	2.382
0.2107	2.418	0.3420	3.219	0.5026	3.421	0.7874	1.997
0.2227	2.497	0.3604	3.311	0.5264	3.367	0.8475	1.478
0.2361	2.593	0.3809	3.366	0.5525	3.296	0.9174	0.7836
(1–x)*o*-chlorofluorobenzene+x*m*-chlorofluorobenzene							
0.08825	7.343	0.4038	23.04	0.5101	24.21	0.6345	22.98
0.1621	12.79	0.4363	23.59	0.5156	24.39	0.6756	21.93
0.2250	16.62	0.4646	23.77	0.5364	24.25	0.7225	20.31
0.2791	19.16	0.4655	23.91	0.5373	24.40	0.7763	17.84
0.3261	20.96	0.4863	24.00	0.5656	23.98	0.8389	14.27
0.3673	22.26	0.4918	24.26	0.5980	23.59	0.9124	8.62

Table 2 Continued

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
(1–x)*o*-bromofluorobenzene+x*m*-bromofluorobenzene							
0.08399	8.935	0.3909	28.68	0.5614	30.44	0.8366	18.39
0.1549	15.34	0.4231	29.45	0.5939	30.17	0.9110	10.95
0.2157	19.82	0.4521	30.07	0.6305	29.43		
0.2683	23.18	0.4783	30.44	0.6719	28.07		
0.3143	25.58	0.5021	30.64	0.7191	26.20		
0.3549	27.42	0.5238	30.68	0.7734	23.10		
(1–x)*o*-fluoroiodobenzene+x*m*-fluoroiodobenzene							
0.08989	12.46	0.3721	36.20	0.5207	39.38	0.7124	32.78
0.1649	20.89	0.4087	37.66	0.5423	39.27	0.7676	28.48
0.2285	26.64	0.4414	38.57	0.5860	37.89	0.8321	22.57
0.2832	30.94	0.4706	39.09	0.6229	36.80	0.9083	13.92
0.3305	34.13	0.4969	39.35	0.6646	35.20		
(1–x)*o*-fluoromethoxybenzene+x*m*-fluoromethoxybenzene							
0.08731	9.661	0.3646	29.68	0.5127	32.87	0.7111	27.98
0.1605	16.37	0.4010	30.85	0.5344	32.94	0.7665	24.47
0.2229	21.53	0.4335	31.73	0.5845	32.68	0.8312	19.31
0.2767	25.25	0.4626	32.29	0.6214	31.83	0.9078	11.60
0.3235	27.89	0.4889	32.59	0.6632	30.35		
(1–x)*o*-fluoronitrobenzene+x*m*-fluoronitrobenzene							
0.04713	1.013	0.2835	3.330	0.5340	2.758	0.7746	1.488
0.09002	1.684	0.3309	3.324	0.5631	2.633	0.8375	1.166
0.1292	2.105	0.3724	3.305	0.5956	2.408	0.9116	0.6710
0.1651	2.509	0.4091	3.202	0.6322	2.250		
0.1982	2.901	0.4417	3.078	0.6734	2.037		
0.2288	3.161	0.5077	2.843	0.7205	1.794		
(1–x)*o*-aminofluorobenzene+x*m*-aminofluorobenzene							
0.08648	–7.265	0.3985	–21.22	0.5653	–20.96	0.8387	–11.42
0.1591	–12.22	0.4309	–21.56	0.5978	–20.44	0.9123	–6.538
0.2211	–15.56	0.4600	–21.72	0.6345	–19.68		
0.2746	–17.94	0.4863	–21.77	0.6754	–18.46		
0.3212	–19.47	0.5101	–21.69	0.7223	–16.91		
0.3622	–20.53	0.5318	–21.52	0.7762	–14.64		

The coefficients A_i in Eq. (1) and standard deviations of the fits s_f:

$$s_f = \left[\sum_{i=1}^{n} H^E\{(\text{obs.}) - H^E(\text{calc.})\}_i^2/(n-k)\right]^{1/2} \qquad (2)$$

are given in Table 3. And the calculated values using Eq. (1) with the coefficients of Table 3 are plotted in Fig. 1. Excess enthalpies of previous reported results [3] of *o*-dimethylbenzene+*m*-dimethylbenzene results showed also good agreements with in 0.3%.

The experimental results for the excess enthalpies of structural isomers showed small enthalpy change on mixing. Excess enthalpies of *o*- and *m*-isomers of aminofluorobenzene, dibromobenzene and iodomethylbenzene showed small negative but other 14 binary mixtures of isomers were positive over the whole range of mole fractions. Those of dimethoxybenzenes showed the largest enthalpic instability but those of aminofluorobenzenes showed the largest enthalpic stability. The mixtures of all homo-substituted structural isomers showed enthalpic instability. Also those of hetero-substituted structural isomers showed positive enthalpy but three mixtures showed negative enthalpies over the whole range of mole fractions.

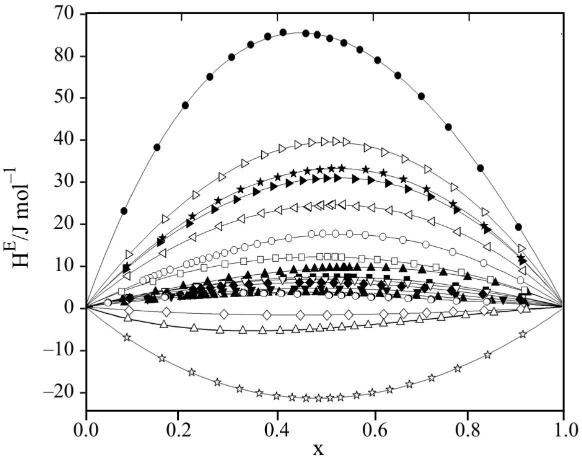

Fig. 1 Enthalpies of mixing of (1–*x*)*o*-isomer+*xm*-isomer at 298.15 K: □ – dimethylbenzene; ■ – diethylbenzene; ● – dimethoxybenzene; ○ – difluorobenzene; ▲ – dichlorobenzene; △ – dibromobenzene; ▼ – fluoromethylbenzene; ▽ – chloromethylbenzene; ◆ – bromomethylbenzene; ◇ – iodomethylbenzene; ◀ – methoxymethylbenzene; ◁ – chlorofluorobenzene; ▶ – bromofluorobenzene; ▷ – iodofluorobenzene; ✩ – fluoromethoxybenzene; ❍ – fluoronitrobenzene; ★ – aminofluorobenzene

There are two descriptions in terms of the difference in the sign of enthalpy changes observed upon the mixing of two structural isomers. One is the effect of molecular packing in the liquid-state; i.e., the change of molar volumes between the *o*-isomers liquid and the *m*-isomers liquid on mixing. The contraction in volume on the mixing of two compounds leads to enthalpic stabilization, and vice versa except in special cases. The other is a difference in the interaction energy between the *o*-isomers and *m*-isomers molecular assembly in pure liquid and mixtures.

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies at infinite dilutions were determined from Eq. (1) with the coefficients in Table 3, and are summarized in Table 4. The limiting excess partial molar enthalpies of 10 *o*-isomers, $H_\mathrm{o}^{\mathrm{E},\infty}$, studied were larger than those of *m*-isomers, $H_\mathrm{o}^{\mathrm{E},\infty}$, and 7 other systems were vice versa.

The structural isomers systems have two substituted groups and phenyl groups. The two substituted groups of structural isomers can have two opposite effects on the π-electron of the phenyl group and the molecular properties of isomers. There might be no small dipole–dipole interactions and dipole–induced dipole interaction effects on the limiting excess partial molar enthalpies of the mixtures. The dipole–dipole and dipole–induced dipole interaction energy of pair molecules [18] are shown as:

$$u_{12} = -\frac{2\mu_1^2\mu_2^2}{3r^6kT} \tag{3}$$

$$u_{12} = -\frac{\alpha_2\mu_1^2 + \alpha_1\mu_2^2}{r^6} \tag{4}$$

where α, μ, *r* and *k* are polarizability, dipole moment, distance between molecules and Boltzmann coefficient, respectively. The molecular shapes of the isomers are not spherical, but as a first approach, all molecules were treated as spherical molecules. The values of *r* for each system were calculated by

Table 3 Best fits coefficients of Eq. (1)

Mixtures of *o*- and *m*-isomers	A_1	A_2	A_3	s_f/J mol^{-1}
Dimethylbenzene	47.48	1.03	7.63	0.15
Diethylbenzene	28.44	–1.09	–2.18	0.06
Dimethoxybenzene	258.12	53.88	7.35	0.23
Difluorobenzene	90.37	–1.59	15.53	0.47
Dichlorobenzene	36.81	–12.02	3.29	0.17
Dibromobenzene	–20.29	–15.32	–2.04	0.03
Fluoromethylbenzene	17.56	1.23	–2.51	0.04
Chloromethylbenzene	26.26	1.89	0.76	0.10
Bromomethylbenzene	22.98	2.40	–1.49	0.05
Iodomethylbenzene	–7.67	–2.15	–0.31	0.05
Methoxymethylbenzene	13.71	2.46	–1.27	0.02
Chlorofluorobenzene	96.84	–7.47	6.17	0.12
Bromofluorobenzene	122.52	–12.59	6.54	0.07
Fluoroiodobenzene	156.65	–7.14	–0.57	0.24
Fluoromethoxybenzene	131.49	–12.17	–2.44	0.15
Fluoronitrobenzene	11.63	8.06	4.27	0.06
Aminofluorobenzene	–86.75	–6.34	–1.47	0.09

Table 4 Limiting excess partial molar enthalpies at 298.15 K

Mixtures of *o*- and *m*-isomers	$H_o^{E,\infty}$/J mol^{-1}	$H_m^{E,\infty}$/J mol^{-1}
Dimethylbenzene	54.08	56.14
Diethylbenzene	27.35	25.16
Dimethoxybenzene	211.6	319.4
Difluorobenzene	107.5	104.3
Dichlorobenzene	52.12	28.08
Dibromobenzene	–7.00	–37.65
Fluoromethylbenzene	13.81	16.28
Chloromethylbenzene	25.13	28.91
Bromomethylbenzene	19.08	23.89
Iodomethylbenzene	–5.83	–10.13
Methoxymethylbenzene	9.98	14.91
Chlorofluorobenzene	110.5	95.55
Bromofluorobenzene	141.7	116.5
Fluoroiodobenzene	163.2	145.0
Fluoromethoxybenzene	141.2	116.9
Fluoronitrobenzene	7.84	23.97
Aminofluorobenzene	–81.87	–94.56

(r_0+r_m). Here r_0 and r_m were the molecular radius of *o*- and *m*-isomer calculated from the densities in the first column of Table 1, respectively.

All of dipole moments or other physicochemical properties of *o*- and *m*-isomers have been not reported. The dipole moments and other physicochemical properties of *o*- and *m*-isomers were calculated by HyperChem [19] after geometrical optimization of the molecular shapes of these isomers as shown in Table 1. Geometrical optimization of the molecular shapes of these isomers was carried out by calculations using the Gaussian method [20] and Molecular Modeling Pro [21]. And ab initio calculations on molecules were performed at the RHF/6-311G level of theory.

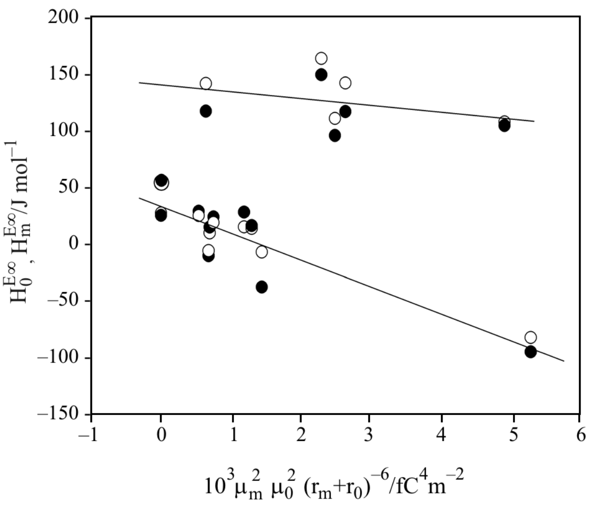

Fig. 2 Correlation between $H_i^{E,\infty}$ and dipole–dipole interaction energy: ● – $H_1^{E,\infty}$; ○ – $H_2^{E,\infty}$

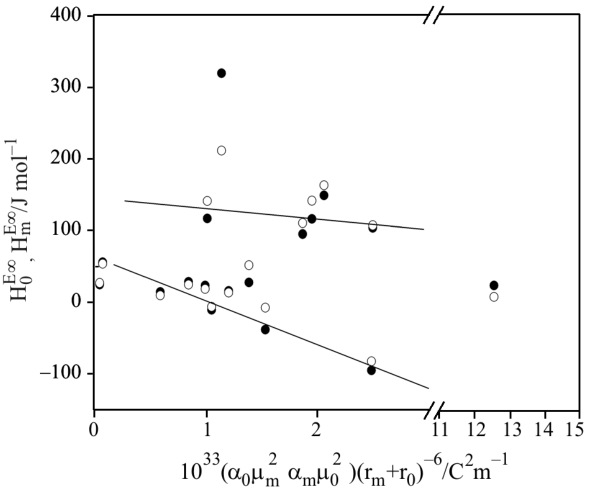

Fig. 3 Correlation between $H_i^{E,\infty}$ and dipole–induces dipole interaction energy: ● – $H_1^{E,\infty}$; ○ – $H_2^{E,\infty}$

Correlations between partial molar enthalpies at infinite dilution and dipole–dipole interaction and dipole–induced dipole interaction are shown in Figs 2 and 3, respectively. Two linear relationships were obtained as shown in Figs 2 and 3. Partial molar enthalpies at infinite dilution decreased with increasing stabilization by dipole–dipole or dipole–induced dipole interaction between *o*-isomers and *m*-isomers. The coefficients of Eq. (5) and the standard deviations are listed in Table 5.

$$H^{E,\infty}/\text{kJ mol}^{-1} = a + b\xi \tag{5}$$

where

$$\xi = \frac{\mu_1^2\mu_2^2}{(r_1 + r_2)^6}$$

or

$$\xi = \frac{\alpha_2\mu_1^2 + \alpha_1\mu_2^2}{(r_1 + r_2)^6}$$

for dipole–dipole or dipole induced–dipole interaction term, respectively.

The upper line belongs to all binary mixtures that have fluoro substituted isomers and the lower line's group belongs to all binary mixtures that have methyl substituted isomers in Figs 2 and 3, respectively. The fluoro and methyl group might have an opposite effect on the π electron cloud of phenyl groups. The so-called induced and resonance effects had opposite effects on the phenyl group.

The correlation between excess enthalpies and differences of pure *o*-isomers and *m*-isomers interaction of dipole–dipole or dipole–induced dipole interaction are shown in Figs 4 and 5, respectively. When dipole–dipole interactions between pure *m*-isomers were larger than those of *o*-isomers, enthalpic stabilization increased except in a few systems as shown in Fig. 5. A similar relation was also found in Fig. 6 for the dipole-induced dipole interaction term.

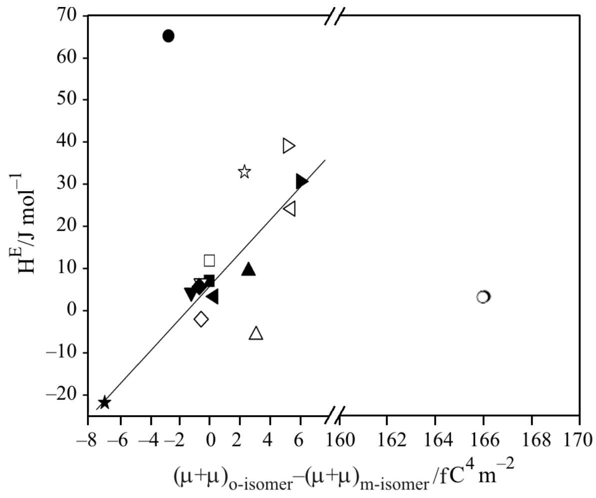

Fig. 4 Correlation between excess enthalpies and the difference of dipole–dipole interaction energy of *o*-isomer and *m*-isomer: □ – dimethylbenzene; ■ – diethylbenzene; ● – dimethoxybenzene; ○ – difluorobenzene; ▲ – dichlorobenzene; △ – dibromobenzene; ▼ – fluoromethylbenzene; ▽ – chloromethylbenzene; ◆ – bromomethylbenzene; ◇ – iodomethylbenzene; ◀ – methoxymethylbenzene; ◁ – chlorofluorobenzene; ▶ – bromofluorobenzene; ▷ – iodofluorobenzene; ☆ – fluoromethoxybenzene; ❍ – fluoronitrobenzene; ★ – aminofluorobenzene

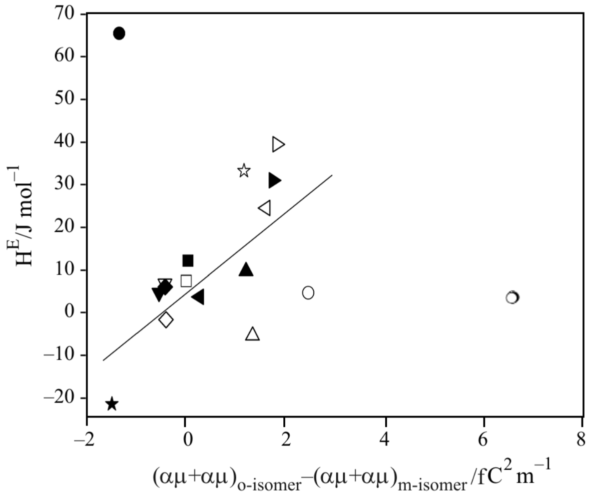

Fig. 5 Correlation between excess enthalpies and the difference of dipole–induced dipole interaction energy of *o*-isomer and *m*-isomer: □ – dimethylbenzene; ■ – diethylbenzene; ● – dimethoxybenzene; ○ – difluorobenzene; ▲ – dichlorobenzene; △ – dibromobenzene; ▼ – fluoromethylbenzene; ▽ – chloromethylbenzene; ◆ – bromomethylbenzene; ◇ – iodomethylbenzene; ◀ – methoxymethylbenzene; ◁ – chlorofluorobenzene; ▶ – bromofluorobenzene; ▷ – iodofluorobenzene; ☆ – fluoromethoxybenzene; ❍ – fluoronitrobenzene; ★ – aminofluorobenzene

Four isomers in which enthalpies were increased with increasing entropies of vaporization, were hetero-substituent compounds and have substituents of fluoro except dimethoxybenzene. The geometrical viewpoint of the bond dipole for structural isomers, *o*-isomers of dipole moment and induced dipole moments of homo-substituents are larger than those of *m*-isomers. Also, structural isomers that have hetero-substituents were almost the same when those substituents were the same category of polarity or other properties, although not all of them. Some substituents had an opposite effect on the π-electron cloud and molecular properties. Some dipole–dipole or dipole–induced dipole interaction energies of

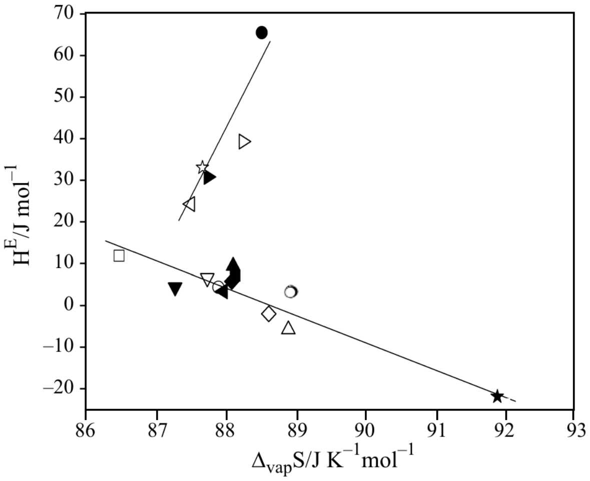

Fig. 6 Correlation between excess enthalpies of stractural isomers mixtures and entropies of vaporization: □ – dimethylbenzene; ■ – diethylbenzene; ● – dimethoxybenzene; ○ – difluorobenzene; ▲ – dichlorobenzene; △ – dibromobenzene; ▼ – fluoromethylbenzene; ▽ – chloromethylbenzene; ◆ – bromomethylbenzene; ◇ – iodomethylbenzene; ◀ – methoxymethylbenzene; ◁ – chlorofluorobenzene; ▶ – bromofluorobenzene; ▷ – iodofluorobenzene; ☆ – fluoromethoxybenzene; ❍ – fluoronitrobenzene; ★ – aminofluorobenzene

Table 5 Coefficients of Eq. (5) and the standard deviations of the fits

a	*b*	s_f	ξ
75.3	$-16.8\cdot10^3$	10.0	$\mu_1^2\mu_2^2/(r_1+r_2)^6$
8.1	$-5.1\cdot10^3$	5.0	$\mu_1^2\mu_2^2/(r_1+r_2)^6$
137	$-8.6\cdot10^{23}$	20	$\alpha_2\mu_1^2+\alpha_1\mu_2^2/(r_1+r_2)^6$
67	$-51.0\cdot10^{23}$	32	$\alpha_2\mu_1^2+\alpha_1\mu_2^2/(r_1+r_2)^6$

$H^{E,\infty}$/kJ mol^{-1} = $a + b\xi$ (5). Here $\xi=\mu_1^2\mu_2^2/(r_1+r_2)^6$ or $\xi=\alpha_2\mu_1^2+\alpha_1\mu_2^2/(r_1+r_2)^6$ for dipole–dipole or dipole induced–dipole interaction term, respectively *o*-isomers and *o*-isomers were smaller than those of *m*-isomers and *m*-isomers.

The excess enthalpies of 14 *o*- and *m*-isomer mixtures were endothermic. The major effect on the excess enthalpies of *o*-isomers+*m*-isomers might arise from hindering stable dipolar–dipolar or dipolar–dipolar induced dipole contacts between *o*-isomers by the less polar components of *m*-isomers. However, the mixtures of *o*-isomer+*m*-isomer have not only the effect as polar *o*-isomers from *m*-isomers but additionally, some energetic effect from volume contraction on mixing.

Entropies of vaporization of pure structural isomers are a measure of the association degree of liquid as shown by Trouton's rule. There are two opposite correlations in Fig. 6 between enthalpies and entropies of the vaporization of pure structural isomers as summarized in the following Eqs (6) and (7).

$$\Delta H/\mathrm{J\ mol^{-1}} = 55.5 - 6.3\Delta_\mathrm{V}S,\ s_\mathrm{f} = 3.5\ \mathrm{J\ mol^{-1}} \quad (6)$$

$$\Delta H/\mathrm{J\ mol^{-1}} = -2947.2 + 34.0\Delta_\mathrm{V}S,\ s_\mathrm{f} = 7.3\ \mathrm{J\ mol^{-1}} \quad (7)$$

The groups in which excess enthalpies were increased with increasing entropies of vaporization might have a stronger interaction of the same kind of molecules than that of different-species and vice versa. A large entropy of vaporization shows that molecular motion in the liquid-state is inhibited by intermolecular interaction. This demonstrates that interactions of the pure liquids, which have a large entropy of vaporization, are preferable to those of the hetero-substituent pairs. Thus, enthalpies of the mixing of structural isomers liquids with large entropies of vaporization are more stable than those of liquids with lower entropies of vaporization.

These findings show that the interaction terms of the mixing entropy are different for these two groups. The slopes of correlation were not dissimilar, and only the intercepts of correlation were different. This may arise from the different contribution of entropies on mixing.

References

1 I. Prigogine, The Molecular Theory of Solutions, North-Holland, Amsterdam 1957.
2 T. Kimura and S. Takagi, J. Chem. Thermodyn., 32 (2000) 1257.
3 T. Kimura and S. Takagi, J. Therm. Anal. Cal., 64 (2001) 231.
4 T. Kimura, T. Ozaki and S. Takagi, Chirality, 10 (1998) 722.
5 T. Kimura, T. Ozaki and S. Takagi, Enantiomers, 6 (2001) 5.
6 T. Kimura, T. Matsushita, K. Ueda, T. Matsuda, F. Aktar, T. Kamiyama and M. Fujisawa, Thermochim. Acta, 414 (2004) 209.
7 T. Kimura, M. A. Kahn, M. Ishii, K. Ueda, T. Matsushita, T. Kamiyama and M. Fujisawa, J. Chem. Thermodyn., 38 (2006) 1042.
8 T. Kimura, A. Khan and T. Kamiyama, J. Therm. Anal. Cal., 85 (2006) 559.
9 T. Kimura, A. Khan and T. Kamiyama, Chirality, 18 (2006) 581.
10 T. Kimura, A. Khan and T. Kamiyama, J. Therm. Anal. Cal., 85 (2006) 575.
11 M. Fujisawa and T. Kimura, J. Therm. Anal. Cal., 85 (2006) 589.
12 H. Aki, Y. Okamoto and T. Kimura, J. Therm. Anal. Cal., 85 (2006) 681.
13 T. Kimura, T. Kitai, T. Kamiyama and M. Fujisawa, Thermochim. Acta, 450 (2006) 91.
14 J. Singh, H. D. Pflug and D. C. Benson, J. Phys. Chem., 72 (1968) 1939.
15 V. T. Lam, S. Murakami and G. C. Benson, J. Chem. Thermodyn., 2 (1970) 17.
16 T. Kimura, Y. Usui, S. Nishimura and S. Takagi, J. Fac. Sci. Technol., Kinki Univ., 25 (1983) 109.
17 T. Kimura, T. Ozaki, Y. Nakai, K. Takeda and S. Takagi, J. Thermal Anal., 54 (1998) 285.
18 K. Shinoda, 'Principles of Solution and Solubilities', Marcel Dekker, 1978.
19 HyperChem version 7.01, HYPERCUBE, Inc.
20 Gaussian 03, Revision B.03, Gaussian, Inc., Pittsburgh PA 2003.
21 Molecular Moldeling Pro, NorGwyn Montgomery Software Inc.
22 J. A. Riddick, W. B. Bunger and T. K. Sakano,'Organic Solvent', John Wiley & Sons, New York 1986.

DOI: 10.1007/s10973-006-8230-x