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Excess enthalpies of binary mixtures of *ortho*-, *meta*-, and *para*-structural isomers

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Abstract The excess molar enthalpies of 8 binary mixtures for the *o*-, *m*-, and *p*-isomers of fluoroiodobenzene, fluoromethoxybenzene, bromofluorobenzene, chlorofluorobenzene, difluorobenzene, fluoromethylbenzene, fluoronitrobenzene, and aminofluoro-benzene were measured at 298.15 K. The changes of the measured enthalpies were very small. The experimental results revealed that the isomers containing two electron-acceptor groups showed the most positive excess enthalpy change, while isomers containing both one electron donor and one electron acceptor group, such as aminofluorobenzene, showed more stable and always the most negative results.

Keywords Excess enthalpy · Structural isomers · Interaction energies of dipole · Induced dipole · Quadrupole

Introduction

It is important to show how the molecules constitute a solution in a liquid state mutually recognize each other to understand various reactions. Most interactions of optical isomers, structural, and isotopic isomerism are unclear. Clarifying the thermodynamic properties of a solution by the differences in the molecular structure is of fundamental importance. 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 have been discussed [4–11].

From the viewpoint of the mutual interaction of isomers, Benson and co-workers [12, 13] reported excess enthalpies of the *o*-, *m*-, and *p*-isomers of dimethyl-benzene. In a previous study [14], to obtain systematic information for the effect of structural isomerism in the solution state on the molecular interaction, the excess enthalpies of 17 binary mixtures of *o*- and *m*-isomers were determined. In this study, to obtain further systematic information on the positional effects of structural isomerism in the solution state on the intermolecular interaction, the excess enthalpies of eight binary mixtures of *o*- and *p*-isomers and *m*- and *p*-isomers were determined at 298.15 K.

Experimental

Materials

The *o*-, *m*-, and *p*-isomers of fluoroiodobenzene (FIB), fluoromethoxybenzene (FMOB), bromofluorobenzene (BFB), chlorofluorobenzene (CFB), difluorobenzene (DFB), fluoromethylbenzene (FMB), fluoronitrobenzene (FNB), and aminofluoro-benzene (AFB) used in this study were

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supplied by Tokyo Kasei and purified with freshly activated molecular sieves of 4 Å to remove all traces of moisture and stored until use. These isomers were activated by evacuating at 498.15 K for 6 h under 10^{-2} to 10^{-3} Pa.

Apparatus

The excess molar enthalpies for *o*-, *m*-, and *p*-isomers were measured by a twin-microcalorimeter of the heat-conduction type of a Thermal Activity Monitor (Thermometric AB, Järfälla, Sweden) with a ca. 1-cm^3 mixing vessel, which was modified by us, and the procedures are described in detail in a previous study [15]. To ensure the accuracy and precision of the calorimeter for small enthalpy change, the excess enthalpies of (*o*-xylene + *m*-xylene) were measured at 298.15 K, and the results agree well with those of a previous study [3]. The densities of the samples were measured using a vibrating-tube densitometer (Anton Paar DMA55) [16] and the results of the densities are listed in Table 1 with the values for the physical properties of all the isomers.

Results and discussion

The observed excess molar enthalpies (*o*- and *p*-isomers) and (*m*- and *p*-isomers) at 298.15 K are listed in Tables 2 and 3, respectively. The observed values were fitted with the Redlich–Kister type equation:

$$H_m^{\mathrm{E}} = x(1-x)\sum_{i=1}^{k} A_i(1-2x)^{i-1} \tag{1}$$

The coefficients A_i in Eq. 1 and the standard deviations of the fits s_{f}

$$s_{\mathrm{f}} = \left[\sum_{i=1}^{n}\{H^{\mathrm{E}}(\mathrm{obs.}) - H^{\mathrm{E}}(\mathrm{calc.})\}_i^2/(n-k)\right]^{1/2} \tag{2}$$

are given in Table 4. The experimental results and smoothing curves from Eq. 1 with the coefficients of Table 4 are plotted in Figs. 1 and 2; the excess enthalpies for (*o*- and *m*-isomers) [14] are plotted in Fig. 3 for comparison.

All the observed results for the excess molar enthalpies of isomers are very small. Excess enthalpies for (*o*- and *m*-isomers) of AFB were slightly negative but positive for

Table 1 Physicochemical properties of *o*-, *m*-, and *p*-isomers at 298.15 K

Samples	ρ(obs)/g cm^{-3}	10^{30} μ/C m	10^{38} Q/C m^2	10^{39} α/C^2 m^2 J^{-1}
o-Fluoroiodobenzene	1.9230	2.93	−2.47	2.21
m-Fluoroiodobenzene	1.9037	1.78	−2.46	2.19
p-Fluoroiodobenzene	1.9001	0.24	−2.49	2.23
o-Fluoromethoxybenzene	1.1232	3.44	−1.90	1.75
m-Fluoromethoxybenzene	1.1069	3.08	−1.99	1.80
p-Fluoromethoxybenzene	1.1109	2.73	−2.10	1.75
o-Bromofluorobenzene	1.6043	3.83	−2.08	1.90
m-Bromofluorobenzene	1.5871	2.44	−2.19	1.89
p-Bromofluorobenzene	1.5936	0.89	−2.33	2.65
o-Chlorofluorobenzene	1.2344	4.03	−1.88	1.72
m-Chlorofluorobenzene	1.2245	2.48	−1.98	1.71
p-Chlorofluorobenzene	1.2262	0.73	−2.14	2.47
o-Difluorobenzene	1.1629	2.95	−1.58	1.36
m-Difluorobenzene	1.1510	1.71	−1.62	1.36
p-Difluorobenzene	1.1630	0.01	−1.75	1.36
o-Fluoromethylbenzene	0.9985	2.51	−1.70	1.71
m-Fluoromethylbenzene	0.9920	3.06	−1.70	1.68
p-Fluoromethylbenzene	0.9920	3.19	−1.73	1.65
o-Fluoronitrobenzene	1.3290	6.57	−2.18	1.88
m-Fluoronitrobenzene	1.3205	6.13	−2.29	1.75
p-Fluoronitrobenzene	1.3260	4.30	−2.66	1.77
o-Aminofluorobenzene	1.1477	1.65	−1.71	1.53
m-Aminofluorobenzene	1.5165	2.92	−1.71	1.56
p-Aminofluorobenzene	1.1527	3.26	−1.71	1.56

ρ density, μ dipole moment, Q quadrupole moment, α polarizability: dipole moments, quadrupole moments, and polarizabilities were calculated from Gaussian 03 (MP2/6-311G(d,p) polar) [17]

Table 2 Excess enthalpies of $(1 - x)o$-isomer + xp-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}
$(1 - x)o$-Fluoroiodobenzene + xp-fluoroiodobenzene							
0.0799	7.108	0.4098	28.97	0.5649	33.27	0.8539	20.91
0.1479	12.68	0.4386	29.96	0.5936	33.28	0.8851	18.41
0.2066	17.19	0.4646	30.69	0.6254	32.78	0.9212	12.83
0.2577	20.74	0.4884	31.33	0.6608	32.24	0.9277	12.31
0.3026	23.49	0.4934	31.6	0.7004	31.18	0.9390	10.61
0.3424	25.75	0.5151	32.52	0.7450	29.19	0.9625	6.551
0.3779	27.52	0.5389	32.91	0.7957	25.88		
$(1 - x)o$-Fluoromethoxybenzene + xp-fluoromethoxybenzene							
0.0801	−3.630	0.3786	−13.43	0.5760	−15.03	0.7725	−12.01
0.1483	−6.514	0.4105	−13.95	0.6015	−14.96	0.8191	−10.22
0.2071	−8.752	0.4393	−14.33	0.6293	−14.69	0.8717	−7.910
0.2583	−10.44	0.4654	−14.62	0.6599	−14.36	0.9314	−4.699
0.3032	−11.64	0.4891	−14.92	0.6936	−13.84		
0.3431	−12.64	0.5525	−15.05	0.7309	−13.08		
$(1 - x)o$-Bromofluorobenzene + xp-bromofluorobenzene							
0.0796	6.576	0.4090	29.79	0.5787	35.52	0.8947	18.60
0.1475	12.13	0.4377	31.25	0.6109	35.84	0.9166	16.04
0.2060	16.65	0.4638	32.50	0.6468	35.76	0.9272	13.78
0.2571	20.43	0.4876	33.52	0.6873	35.14	0.9622	7.412
0.3019	23.51	0.4997	33.54	0.7331	33.70		
0.3417	26.07	0.5235	34.28	0.7855	30.78		
0.3772	28.24	0.5497	34.96	0.8460	25.42		
$(1 - x)o$-Chlorofluorobenzene + xp-chlorofluorobenzene							
0.0797	5.750	0.3774	23.92	0.5252	29.16	0.7344	29.20
0.1477	10.50	0.4093	25.35	0.5514	29.81	0.7858	26.70
0.2062	14.19	0.4380	26.57	0.5803	30.44	0.8148	24.78
0.2573	17.43	0.4641	27.57	0.6124	30.88	0.8462	22.08
0.3022	19.93	0.4879	28.46	0.6483	30.83	0.8800	18.92
0.3420	22.20	0.5096	28.47	0.6887	30.54	0.9167	14.43
$(1 - x)o$-Difluorobenzene + xp-difluorobenzene							
0.0162	1.699	0.1336	12.64	0.4465	31.87	0.8588	26.094
0.0319	3.112	0.138	14.32	0.4757	33.19	0.8902	22.122
0.0471	4.454	0.1448	13.56	0.5091	34.52	0.9196	14.539
0.0618	5.672	0.1582	14.78	0.5475	35.56	0.9238	16.239
0.0741	7.403	0.1743	16.14	0.5922	36.55	0.924	16.956
0.0761	6.96	0.194	17.83	0.6448	37.81	0.9581	8.467
0.0900	7.942	0.2187	19.48	0.7076	36.46	0.9605	9.644
0.1033	8.842	0.2507	22.02	0.8021	31.21		
0.1164	9.880	0.2936	24.42	0.8295	29.02		
0.1291	10.88	0.3543	27.05	0.8583	25.25		
$(1 - x)o$-Fluoromethylbenzene + xp-fluoromethylbenzene							
0.0647	−0.133	0.3291	−0.454	0.6161	−0.574	0.8652	−0.32
0.1405	−0.239	0.5169	−0.567	0.6815	−0.542		
0.2464	−0.343	0.5621	−0.585	0.7624	−0.467		
$(1 - x)o$-Fluoronitrobenzene + xp-fluoronitrobenzene							
0.0789	−6.376	0.3754	−20.11	0.5015	−20.46	0.6888	−15.95
0.1466	−10.99	0.4072	−20.65	0.5253	−20.24	0.7345	−14.00

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}
0.2048	−14.46	0.4359	−20.81	0.5515	−19.86	0.7867	−11.56
0.2557	−16.72	0.462	−20.79	0.5804	−19.33	0.8469	−8.344
0.3004	−18.35	0.4857	−20.77	0.6126	−18.56	0.9171	−4.502
0.3400	−19.46	0.5075	−20.53	0.6484	−17.48		
(1 − x)*o*-Aminofluorobenzene + x*p*-aminofluorobenzene							
0.0159	−2.779	0.2215	−28.52	0.4868	−40.23	0.689	−33.78
0.0313	−5.298	0.2751	−33.18	0.5106	−40.07	0.7347	−30.66
0.0463	−7.672	0.3217	−36.37	0.5256	−39.85	0.7869	−26.27
0.0608	−9.963	0.3627	−38.09	0.5517	−39.45	0.8471	−20.2
0.0748	−12.09	0.399	−39.19	0.5807	−38.7	0.8471	−20.2
0.0866	−13.34	0.4314	−39.85	0.6128	−37.61	0.9172	−11.81
0.1595	−22.79	0.4605	−40.26	0.6487	−36.01		

Table 3 Excess enthalpies of (1 − x)*m*-isomer + x*p*-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)*m*-Fluoroiodobenzene + x*p*-fluoroiodobenzene							
0.0800	5.490	0.3783	17.25	0.5233	18.24	0.7072	14.89
0.1481	9.514	0.4101	17.76	0.5470	18.08	0.7512	13.31
0.2068	12.69	0.4389	18.06	0.5729	17.75	0.8010	11.34
0.2580	14.67	0.4650	18.20	0.6015	17.28	0.8579	8.385
0.3029	15.80	0.4888	18.22	0.6330	16.74	0.9235	4.835
0.3427	16.73	0.5015	18.22	0.6680	16.08		
(1 − x)*m*-Fluoromethoxybenzene + x*p*-fluoromethoxybenzene							
0.0791	1.369	0.3754	4.425	0.5431	4.642	0.7482	3.439
0.1466	2.341	0.4072	4.578	0.5691	4.534	0.7985	2.954
0.2049	3.210	0.4360	4.630	0.5978	4.404	0.8560	2.354
0.2557	3.633	0.4620	4.637	0.6294	4.253	0.9224	1.256
0.3004	3.962	0.4858	4.626	0.6646	4.069		
0.3401	4.258	0.5194	4.675	0.7039	3.765		
(1 − x)*m*-Bromofluorobenzene + x*p*-bromofluorobenzene							
0.0822	4.189	0.3855	12.90	0.5406	13.56	0.7463	10.96
0.1520	7.008	0.4175	13.17	0.5666	13.52	0.7968	9.450
0.2119	8.858	0.4464	13.48	0.5953	13.31	0.8547	7.470
0.2638	10.38	0.4726	13.65	0.6270	13.12	0.9217	4.658
0.3094	11.62	0.4964	13.69	0.6623	12.62		
0.3496	12.41	0.5168	13.74	0.7018	11.84		
(1 − x)*m*-Chlorofluorobenzene + x*p*-chlorofluorobenzene							
0.0816	3.857	0.3834	12.36	0.5652	13.75	0.7959	9.385
0.1508	6.827	0.4154	12.82	0.5939	13.59	0.8540	7.312
0.2104	8.656	0.4442	13.06	0.6256	13.13	0.9212	4.365
0.2621	10.09	0.4936	13.65	0.6610	12.51		
0.3075	11.11	0.5154	13.91	0.7005	11.77		
0.3476	11.89	0.5391	13.87	0.7452	10.72		
(1 − x)*m*-Difluorobenzene + x*p*-difluorobenzene							
0.0664	2.526	0.3594	12.72	0.5361	14.71	0.7663	9.433
0.0670	2.381	0.3648	12.71	0.5513	14.50	0.7815	8.948

Table 3 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}
0.1245	4.553	0.3928	13.43	0.5851	14.0	0.7948	8.514
0.1255	4.559	0.3951	13.78	0.6142	13.48	0.8066	8.109
0.1758	6.174	0.4185	14.02	0.6395	12.89	0.8172	7.749
0.1772	6.323	0.4421	14.45	0.6616	12.29	0.8266	7.409
0.2214	7.434	0.4638	14.70	0.6812	11.69	0.8351	7.087
0.2230	7.759	0.4839	14.83	0.6987	11.21	0.8753	6.618
0.2736	9.432	0.5026	14.94	0.7143	10.77	0.8753	6.046
0.3192	11.12	0.5199	14.89	0.7284	10.45	0.9335	2.059
$(1-x)$*m*-Fluoromethylbenzene + x*p*-fluoromethylbenzene							
0.0425	0.0334	0.3671	0.2341	0.6116	0.2494	0.9250	0.0576
0.0815	0.0666	0.4361	0.2535	0.7025	0.2217	0.9611	0.0285
0.1175	0.0958	0.4915	0.2616	0.8253	0.1412		
0.1620	0.1226	0.5370	0.2642	0.8605	0.1098		
0.2788	0.1923	0.5415	0.2675	0.8916	0.0894		
$(1-x)$*m*-Fluoronitrobenzene + x*p*-fluoronitrobenzene							
0.0793	0.670	0.3767	2.470	0.5641	2.824	0.7952	2.056
0.1472	1.186	0.4085	2.576	0.5928	2.794	0.8535	1.571
0.2057	1.587	0.4372	2.652	0.6246	2.739	0.9209	0.912
0.2567	1.899	0.4633	2.703	0.6600	2.628		
0.3015	2.141	0.5143	2.805	0.6997	2.506		
0.3412	2.328	0.5381	2.847	0.7444	2.357		
$(1-x)$*m*-Aminofluorobenzene + x*p*-aminofluorobenzene							
0.0811	−15.93	0.3463	−48.78	0.4927	−54.14	0.6339	−48.06
0.1501	−27.27	0.382	−50.87	0.5145	−53.21	0.6840	−44.31
0.2094	−35.53	0.4140	−52.56	0.5197	−53.12	0.7427	−38.84
0.2610	−41.41	0.4428	−53.37	0.5529	−52.23	0.8123	−30.58
0.3063	−45.75	0.4689	−53.90	0.5907	−50.59	0.8965	−18.35

the other seven binary mixtures of isomers, and the results fall in the sequence of maximum to minimum: FIB > FMOB > BFB > CFB > DFB > FMB > FNB > AFB. The excess enthalpies of FMB, FMOB, FNB, and AFB for (*o*- and *p*-isomers) binary systems were slightly negative, whereas the other four systems were positive. For the (*m*- and *p*-isomers) systems, FIB was the most positive and AFB the most negative, the same as the (*o*- and *m*-isomers) systems. And also only AFB was negative while the other seven systems were positive. The sequence stabilization of the binary systems of (*o*- and *p*-isomers) and (*m*- and *p*-isomers) was: DFB > BFB > FIB > CFB > FMB > FMOB > FNB > AFB and FIB > DFB > CFB > BFB > FMOB > FNB > FMB > AFB, respectively as shown in Figs. 1 and 2, respectively.

All the structural isomers are phenyl-containing compounds, and contain two substituted groups; one of the two substituted groups is fluorine and the other is –I, –Br, –Cl, –F, –O–CH$_3$, –CH$_3$, –NO$_2$, and –NH$_2$ for the eightisomers. A different substituted group has two opposite effects on the π-electron of the benzene ring: electron donor and electron acceptor, which increase and decrease the electron density of the benzene ring, respectively. Two types of isomer groups were obtained according to the different effect of the substituted groups: group one including FIB, BFB, CFB, and DFB, all of which contained two electron–acceptor groups, the most electronegative of which is halogen and which showed the most positive excess enthalpy change.

FMOB, FMB, FNB, and AFB are the second group that contains both one electron donor and one electron acceptor group and has less enthalpy change, as the experimental results shown in Figs. 1, 2, and 3.

The excess partial molar enthalpies for all the isomer systems at infinite dilution were determined from Eq. 1 with the coefficients in Table 4, and are summarized in Table 5. A few of the excess partial molar enthalpies for $\left(H_o^{\mathrm{E},\infty}, H_m^{\mathrm{E},\infty}\right)$, $\left(H_o^{\mathrm{E},\infty}, H_p^{\mathrm{E},\infty}\right)$, and $\left(H_m^{\mathrm{E},\infty}, H_p^{\mathrm{E},\infty}\right)$ are negative.

Table 4 Best fits coefficients A_i of Redlich–Kister type Eq. 1 with standard deviation of the fits s_f. for (*o*- and *p*-isomers) and (*m*- and *p*-isomers)

Samples	A_1	A_2	A_3	s_f/J mol^{-1}
Mixtures of *o*- and *p*-isomers				
Fluoroiodobenzene	127.6	−47.83	15.47	0.24
Fluoromethoxybenzene	−59.74	12.90	−2.85	0.06
Bromofluorobenzene	135.03	−68.35	20.63	0.21
Chlorofluorobenzene	114.59	−62.10	27.48	0.18
Difluorobenzene	137.80	−72.94	43.55	0.64
Fluoromethylbenzene	−2.25	0.61	−0.15	0.01
Fluoronitrobenzene	−82.44	−17.04	12.21	0.06
Aminofluorobenzene	−160.9	−10.27	−4.09	0.14
Mixtures of *m*- and *p*-isomers				
Fluoroiodobenzene	73.08	4.20	0.62	0.13
Fluoromethoxybenzene	18.62	0.83	0.25	0.05
Bromofluorobenzene	54.70	−3.81	4.96	0.09
Chlorofluorobenzene	54.45	−5.29	1.08	0.16
Difluorobenzene	58.18	−4.76	−27.44	0.37
Fluoromethylbenzene	1.26	−0.19	0.61	0.54
Fluoronitrobenzene	11.13	−2.33	−0.19	0.02
Aminofluorobenzene	−213.70	−12.83	17.44	0.31

$$H_m^{\mathrm{E}} = x(1-x)\sum_{i=1}^{k} A_i(1-2x)^{i-1}$$

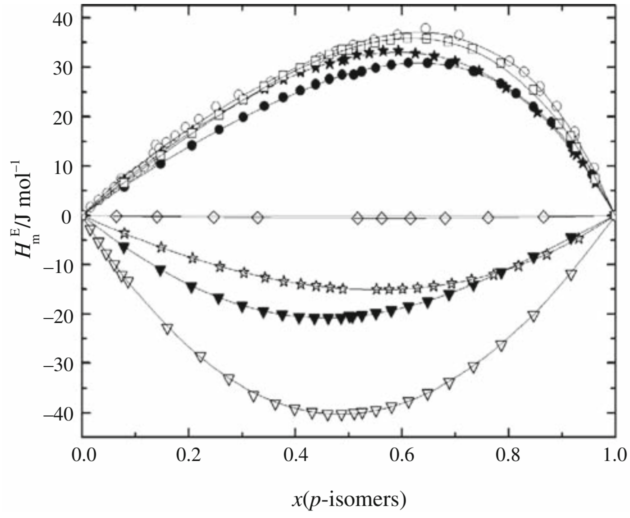

Fig. 1 Excess enthalpies of *o*- and *p*-isomers at 298.15 K: *filled star* FIB, *open star* FMOB, *open square* BFB, *filled circle* CFB, *open circle* DFB, *open diamond* FMB, *inverted filled triangle* FNB, *inverted open triangle* AFB

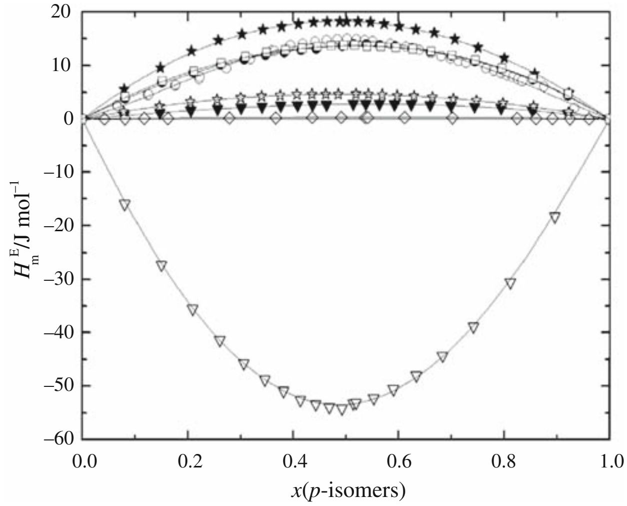

Fig. 2 Excess enthalpies of *m*- and *p*-isomers at 298.15 K: *filled star* FIB, *open star* FMOB, *open square* BFB, *filled circle* CFB, *open circle* DFB, *open diamond* FMB, *inverted filled triangle* FNB, *inverted open triangle* AFB

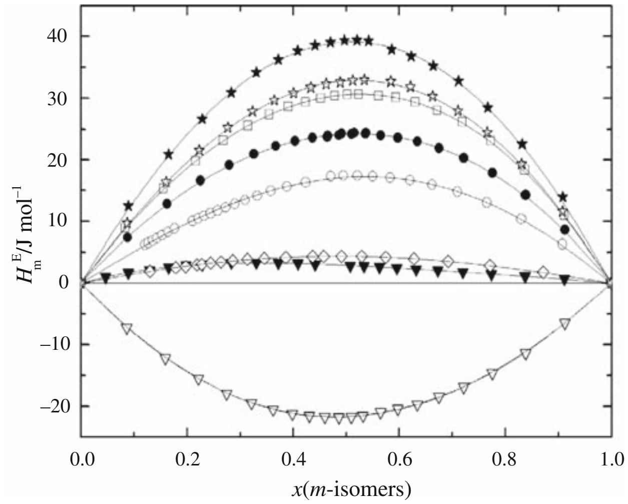

Fig. 3 Excess enthalpies of *o*- and *m*-isomers at 298.15 K [1]: *filled star* FIB, *open star* FMOB, *open square* BFB, *filled circle* CFB, *open circle* DFB, *open diamond* FMB, *inverted filled triangle* FNB, *inverted open triangle* AFB

Limiting the partial molar enthalpies of four halogenated fluorobenzenes (FIB, BFB, CFB, and DFB) had the following sequence:

Limiting partial molar enthalpies of o-isomers in the mixtures of *o*-isomers + *m*-isomers:

FIB > BFB > CFB > DFB

Those of *o*-isomers in the mixtures of *o*-isomers + *p*-isomers:

DFB > BFB > CFB > FIB

Those of *m*-isomers in the mixtures of *m*-isomers + *p*-isomers:

FIB > BFB > CFB > DFB

Those of *m*-isomers in the mixtures of *o*-isomers + *m*-isomers:

FIB > BFB > DFB > CFB

Those of *p*-isomers in the mixtures of *o*-isomers + *p*-isomers:

DFB > FIB > BFB > CFB

Table 5 Limiting excess partial molar enthalpies at 298.15 K in J mol^{-1}

Systems:	*o*- and *m*-Isomers		*o*- and *p*-Isomers		*m*- and *p*-Isomers	
Mixtures	$H_o^{E,\infty}$	$H_m^{E,\infty}$	$H_o^{E,\infty}$	$H_p^{E,\infty}$	$H_m^{E,\infty}$	$H_p^{E,\infty}$
Fluoroiodobenzene	163.2	145.0	190.9	95.24	69.50	77.90
Fluoromethoxybenzene	141.2	116.9	−75.49	−49.69	18.04	19.70
Bromofluorobenzene	141.6	116.5	224.0	87.31	63.47	55.85
Chlorofluorobenzene	110.4	95.56	204.2	79.97	60.82	50.24
Difluorobenzene	107.5	104.31	254.3	108.4	35.50	25.98
Fluoronitrobenzene	23.96	7.84	−53.19	−87.27	13.27	8.61
Fluoromethylbenzene	13.82	16.28	−3.01	−1.79	2.06	1.68
Aminofluorobenzene	−81.88	−94.56	−154.7	−175.3	−183.4	−209.1

Those of *p*-isomers in the mixtures of *m*-isomers + *p*-isomers:
FIB > BFB > CFB > DFB.

The sequence of limiting the partial molar enthalpies of *o*-isomer in the mixtures of *o*-isomers + *m*-isomers and those of *p*-isomer in the mixtures of *m*-isomers + *p*-isomers was the same.

FIB, DFB had the minimum and maximum dipole moment, respectively, among the four halogenated fluorobenzenes (FIB, BFB, CFB, and DFB). The results showed that when stabilizations by dipole–dipole interaction in the isomer's pair were maximum or minimum, then pair interactions between other dihalogenated compounds could obey the weak sequences of those with intense electro negativity of halogen atoms which were constructed by maximum and minimum dipole moments of dihalogenated benzenes.

Of all the results, the excess molar enthalpies of isomers containing AFB had the most stabilized system on mixing. Quadrupole moment, and polarizability of AFB were no larger than any other. However, the amino proton might lead to the formation of another interaction between the other isomers.

To understand the effect of intermolecular interaction on the partial molar excess enthalpies, the correlation between dipole–dipole, dipole-induced dipole, dipole–quadrupole, quadrupole–quadrupole interaction energy with the partial molar excess enthalpies at infinite dilutions were investigated and are shown in Fig. 4.

The dipole moments, quadrupole moment, polarizability, and other physicochemical properties of *o*-, *m*- and *p*-isomers were calculated using ab initio quantum chemical methods based on the Gaussian programs [17] at the

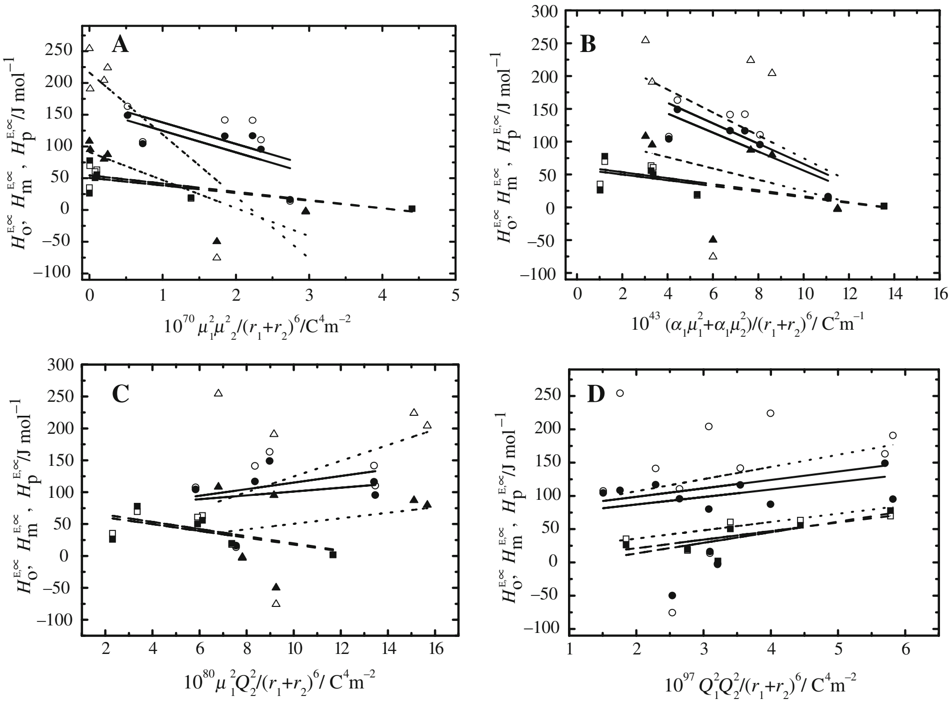

Fig. 4 Correlation between excess enthalpies at infinite dilution and interaction energies of structural isomers for (*o*-isomers + *m*-isomers): *open circle* $H_o^{E,\infty}$, *filled circle* $H_m^{E,\infty}$; for (*o*-isomers + *p*-isomers): *open triangle* $H_o^{E,\infty}$, *filled triangle* $H_p^{E,\infty}$; for (*m*-isomers + *p*-isomers): *open square* $H_m^{E,\infty}$, *filled square* $H_p^{E,\infty}$. **a** Dipole–dipole interaction energies, **b** dipole-induce dipole interaction energies, **c** dipole–quadrupole interaction energies, **d** quadrupole–quadrupole interaction energies. — correlations for (*o*-isomers + *m*-isomers), ……. correlations for (*o*-isomers + *p*-isomers), ———— correlations for (*m*-isomers + *p*-isomers)

MP2/6-311G(d,p) level of theory and Molecular Modeling Pro [18], after geometrical optimization of the molecular shapes of these isomers. As a first approximation, all observed molecules were treated as spherical molecules. The dipole–dipole, dipole-induced dipole, dipole–quadrupole, and quadrupole–quadrupole interaction energy of pair molecules [19] is represented as:

$$u_{12} \propto -\frac{2}{3}\cdot\frac{\mu_1^2\mu_2^2}{r^6kT} \propto \frac{\mu_1^2\mu_2^2}{(r_1+r_2)^6} \tag{3}$$

$$u_{12} \propto -\frac{\alpha_2\mu_1^2+\alpha_1\mu_2^2}{r^6} \propto \frac{\alpha_2\mu_1^2+\alpha_1\mu_2^2}{(r_1+r_2)^6} \tag{4}$$

$$u_{12} \propto -\frac{2}{3}\cdot\frac{\mu_1^2Q_2^2}{r^6kT} \propto \frac{\mu_1^2Q_2^2}{(r_1+r_2)^6} \tag{5}$$

$$u_{12} \propto -\frac{2}{3}\cdot\frac{Q_1^2Q_2^2}{r^6kT} \propto \frac{Q_1^2Q_2^2}{(r_1+r_2)^6} \tag{6}$$

where α, μ, Q, r, and k are polarizability, dipole moment, quadrupole moment, distance between molecules, and Boltzmann coefficient, respectively. The values of r for each system were calculated by ($r_1 + r_2$), and r_1 and r_2 were the molecular radii of the isomers for the binary systems calculated from the densities in the first column of Table 1, respectively.

In comparing $H_o^{\mathrm{E},\infty}$ and $H_p^{\mathrm{E},\infty}$ for the systems of *o*-isomers + *p*-isomers, all dihalogenated compounds and FMOB were deviated from the linear fitting shown as a solid line. They might have other interactions, because they simply obeyed the congener sequence.

And the correlation between interaction energies and partial molar excess enthalpies for all the systems is summarized by Eq. 7.

$$H_1^{\mathrm{E},\infty}, H_2^{\mathrm{E},\infty} = a + b \times u_{12} \tag{7}$$

The coefficients *a*, *b*, and standard deviation are shown in Table 6.

The system including fluoronitrobenzene and aminofluorobenzene showed greater behavioral differences than others, so these were excluded from least squares.

Correlation between infinite dilution and dipole–dipole interaction and dipole-induced dipole interaction of *o*-isomers + *m*-isomers was discussed in a previous paper [14]. Partial molar enthalpies at infinite dilution decreased with increasing stabilization by dipole–dipole, dipole-induced dipole, dipole–quadrupole, or quadrupole–quadrupole interaction between *o*- and *m*-isomers. Partial molar excess enthalpies of the mixtures of *o*-isomers + *p*-isomers, *m*-isomers + *p*-isomers like those of *o*-isomers + *m*-isomers were decreased with the increased interaction energies of dipole–dipole, dipole-induced dipole and dipole–quadrupole, respectively. Those correlations between partial molar excess enthalpies and interaction energies of quadrupole–quadrupole were very small and those of *m*-isomers + *p*-isomers may have weaker opposite slopes than others.

The structural differences of the isomers were one substituted group on the benzene ring in fluoro compounds. The polarizability for the different substituted groups for –I, –Br, —Cl, –F, –O–CH$_3$, –H$_3$, –NO$_2$, and –NH$_2$ were 5.35, 3.05, 2.18, 0.557, 3.29, 2.593, 3.02, and 2.26 (10^{-24} cm^{-3}), respectively[20]. For (*o*- and *m*-isomers) binary systems, the excess enthalpies of the first group decreased with the decreasing order of polarizability of the substituted groups: –I > –Br > –Cl > –F; and also the excess enthalpies of the second group decreased with the decreasing of the polarizability of the substituted groups: –O–CH$_3$ > –NO$_2$ >

Table 6 Best fits coefficients of Eq. 7 and standard deviation of the fits

Systems	*o*(1)-Isomer + *m*(2)-isomer			*o*(1)-Isomer + *p*(2)-isomer			*m*(1)-Isomer + *p*(2)-isomer		
	a	*b*	s_f	*A*	*b*	s_f	*a*	*b*	s_f
Dipole–dipole interaction energy									
$H_1^{\mathrm{E},\infty}$	171	−0.0034	43	216	−0.0098	67	54.7	−0.0013	14
$H_2^{\mathrm{E},\infty}$	216	−0.0034	32	91.0	−0.0044	34	50.6	−0.0012	18
Dipole-induced dipole interaction energy									
$H_1^{\mathrm{E},\infty}$	220	−15.5	34	249	−17.5	124	62.8	−4.59	17
$H_2^{\mathrm{E},\infty}$	201	−14.5	24	110	−8.6	57.	58.6	−4.33	19
Dipole–quadrupole interaction energy									
$H_1^{\mathrm{E},\infty}$	63	5.16	50	1.59	12.3	128	75.9	−5.61	20
$H_2^{\mathrm{E},\infty}$	71	3.0	43	7.32	4.32	62	71.2	−5.33	21
Quadrupole–quadrupole interaction energy									
$H_1^{\mathrm{E},\infty}$	73.4	12.6	49	70.5	18.2	134	−4.34	12.8	21
$H_2^{\mathrm{E},\infty}$	64.5	11.3	41	10.8	12.5	61	−18.3	15.9	17

$H_1^{\mathrm{E},\infty}, H_2^{\mathrm{E},\infty} = a + b \times u_{12}$

Table 7 The absolute difference of dipole moment among *o-*, *m-*, and *p*-isomers

Isomers	$\lvert\mu_o - \mu_m\rvert/10^{30}$ Cm	$\lvert\mu_m - \mu_p\rvert/10^{30}$ Cm	$\lvert\mu_o - \mu_p\rvert/10^{30}$ Cm	Isomers	$\lvert\mu_o - \mu_m\rvert/10^{30}$ Cm	$\lvert\mu_o - \mu_p\rvert/10^{30}$ Cm	$\lvert\mu_m - \mu_p\rvert/10^{30}$ Cm
1st group				2nd group			
Fluoroiodobenzene	1.15	2.69	1.54	Fluoromethylbenzene	0.55	0.12	0.68
Bromofluorobenzene	1.39	2.94	1.55	3rd group			
Chlorofluorobenzene	1.55	3.30	1.75	Fluoronitrobenzene	0.43	1.83	2.27
Difluorobenzene	1.23	2.94	1.70	Aminofluorobenzene	1.28	0.34	1.61
Av	1.33	2.97	1.64	Av	0.86	1.09	1.94
s_f	0.18	0.25	0.11	s_f	0.60	1.05	0.47

Av Average, s_f standard deviation

$-CH_3 > -NH_2$ for (*m*- and *p*-isomers). The absolute difference of dipole moments for $\lvert\mu_o - \mu_m\rvert$, $\lvert\mu_m - \mu_p\rvert$, and $\lvert\mu_o - \mu_p\rvert$ is shown in Table 7.

The difference of dipole moments between *o*- and *m*-isomers, *o*- and *p*-isomers, and *m*- and *p*-isomers was $(1.33 \pm 0.18)\ 10^{-30}$ Cm, $(2.97 \pm 0.25)\ 10^{-30}$ Cm, and $(1.64 \pm 0.11)\ 10^{-30}$ Cm, respectively. The first group had the largest difference in dipole moments when compared to the others, and each dipole moment of the first group was larger than that of the others. The differences for Group 1 were larger and greater than 1, while for Group 2, the absolute dispersion variations were close to 0. The third group of FNB and AFB had a relatively large dipole moment difference but might have other effects. This means that as the difference of the dipole moment between two isomers increased, the change in the excess enthalpies become more positive. This might be due not only to unstabilization by dipole–dipole interaction, but also other effects of mixing of excess volumes because all excess enthalpies were relatively small.

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