J Therm Anal Calorim (2010) 102:1123–1133
DOI 10.1007/s10973-010-0743-7

Excess enthalpies of binary mixtures of *ortho*-, *meta*-, *para*-structural isomers containing aliphatic group

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Received: 11 January 2010 / Accepted: 26 February 2010 / Published online: 21 March 2010

Abstract To obtain further systematic information for the isomer systems, the excess molar enthalpies for binary (*o* + *m*), (*o* + *p*), (*m* + *p*)-isomers of methoxymethylbenzene, ethylmethylbenzene, diethylbenzene, chloromethylbenzene, tolunitrile and fluorobenzonitrile, tolylacetonitrile were measured at 298.15 K. In this article, the results are discussed and compared with those of previous works. The excess enthalpies of binary systems in different solid and liquid states were measured when the pure component of *o*-/*m*-tolunitrile, fluorobenzonitrile was titrated into the prior (*o* + *p*) or (*m* + *p*) mixtures. A series calculation for the interaction energies (*IE*) between the isomers was carried out for the pair molecules by ab initio MO of Gaussian 09. Correlations between the excess enthalpies at a molar fraction of $x = 0.5$ and the intermolecular energy are discussed.

Keywords Excess enthalpies · Structural isomers · Interaction energy

Introduction

The isothermal mixing of (*o* + *m*), (*o* + *p*), (*m* + *p*)-isomers, which show small enthalpy change, can be explained in terms of differences in the intermolecular interaction between pairs of like and unlike molecules, as a result of the slight differences in the isomers structure [1, 2]. Excess molar enthalpies for isotopic systems and enantiomers and solutions of enantiomers, which have slight differences in structure, have been reported and their mutual interactions have been discussed [7–20]. The excess molar enthalpies for fluorine-substituted groups containing isomers of aminofluorobenzene (**F$_1$**), fluoromethoxybenzene (**F$_2$**), difluorobenzene (**F$_3$**), chlorofluorobenzene (**F$_4$**), bromofluorobenzene (**F$_5$**), fluoroiodobenzene (**F$_6$**), fluoronitrobenzene (**F$_7$**), and fluorotoluene (**A$_5$**) have been reported in our previous work [2]. This study examines the structural and thermodynamic properties of mixing of (*o* + *m*), (*o* + *p*), (*m* + *p*)-isomers systems. The excess molar enthalpies for seven alkyl-substituted isomers systems were measured at 298.15 K. Although there are few published papers on the correlations between the structure of isomers and their thermodynamic properties, calculation of the intermolecular interaction energy using the Gaussian method has been the subject of some theoretical studies [3–5] in the gas phase. In this article, the interaction energy (*IE*) of the pair molecules of (*o* + *m*), (*o* + *p*), (*m* + *p*)-isomers are computed by the Gaussian method [6, 23] using the MP2/6-311^{++}G(d,p) basis set.

Experiments

The *o*-, *m*-, *p*-isomers of methoxymethylbenzene (MOMB, **A$_2$**), ethylmethylbenzene (EMB, **A$_3$**), diethylbenzene (DEB, **A$_4$**), chloromethylbenzene (CMB, **A$_6$**), tolunitrile (CNMB, **A$_9$**), and tolylacetonitrile (CCNMB, **A$_{10}$**), fluorobenzonitrile (CNFB, **F$_8$**) (Tokyo Kasei Co. Ltd.) showed in Fig. 1 were maintained with freshly activated molecular sieves 4 Å that evacuated at 498 K for more than 4 h under 10^{-2} to 10^{-3} Pa to remove all traces of moisture.

The heat-conduction microcalorimeter (Thermal Activity Monitor, Thermometic) that was used has been

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

Samples	ρ(obs)/g cm^{-3}	$10^{30}\mu$/C m	10^{38}Q/C m^2	$10^{39}\alpha$/(C^2 m^2 J^{-1})
o-Dimethylbenzene	0.8748	1.56	−1.78	1.72
m-Dimethylbenzene	0.8594	0.85	−1.80	1.88
p-Dimethylbenzene	0.8570	0.24	−1.80	1.96
o-Ethylmethylbenzene	0.8777	1.96	−2.00	1.98
m-Ethylmethylbenzene	0.8603	0.84	−2.02	2.07
p-Ethylmethylbenzene	0.8569	0.38	−2.00	2.17
o-Diethylbenzene	0.8764	1.68	−2.28	2.07
m-Diethylbenzene	0.8598	1.11	−2.28	2.20
p-Diethylbenzene	0.8580	0.16	−2.26	2.35
o-Chloromethylbenzene	1.0770	6.65	−1.98	1.88
m-Chloromethylbenzene	1.0669	8.09	−1.98	1.97
p-Chloromethylbenzene	1.0639	8.61	−1.98	2.08
o-Methoxymethylbenzene	0.9749	5.12	−2.00	1.88
m-Methoxymethylbenzene	0.9675	5.73	−2.01	1.97
p-Methoxymethylbenzene	0.9659	4.54	−1.97	2.16
o-Tolylacetonitrile	1.0061	13.9	−2.61	1.94
m-Tolylacetonitrile	0.9905	15.1	−2.64	2.07
p-Tolylacetonitrile	0.9884	14.7	−2.64	2.18
o-Tolunitrile	0.9884	16.0	−2.13	1.96
m-Tolunitrile	0.9824	17.6	−2.22	2.05
p-Tolunitrile	0.9805	18.5	−2.27	2.19
o-Fluorobenzonitrile	1.1335	19.5	−1.97	1.81
m-Fluorobenzonitrile	1.1346	14.2	−2.22	1.80
p-Fluorobenzonitrile	1.15 ± 0.1[a]	10.9	−2.44	1.84

ρ density, μ dipole moment, Q quadrupole moment, α polarizability

μ, Q, and α were calculated from Gaussian (MP2/6-311G(d,p) polar) [22]

[a] Density of solid state at 293.15 K (From Sicfinder Calculated using Advanced Chemistry Development (ACD/Labs) Software V9.04 for Solaris (© 1994–2009 ACD/Labs))

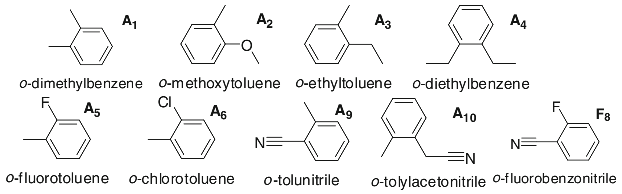

Fig. 1 Structures of *o*-isomers

described previously [1, 2]. The densities of the samples were measured using a vibrating-tube densitometry (Anton Paar DMA55) [20] except those of the *p*-tolunitrile (**A$_9$**) and *p*-fluorobenzonitrile (**F$_8$**), which are solid state at 298.15 K (the melting point is 300 K and 308 K for *p*-tolunitrile (**A$_9$**) [21] and *p*-fluorobenzonitrile (**F$_8$**) [22], respectively). The results of the densities are listed in Table 1 with the values for the physical properties of all the isomers.

Since the *p*-tolunitrile (**A$_9$**) and *p*-fluorobenzonitrile (**F$_8$**) are solid at 298.15 K, the excess enthalpies change for ($o + p$) and ($m + p$)-**A$_9$/F$_8$** cannot be measured directly by mixing the two pure liquids. For this reason, liquid solutions of binary contributions for *op*- and *mp*-**A$_9$/F$_8$** had been preformed at $x_p = 0.8677$, 0.8054 and 0.6905, 0.7747 by the mixing of ($o + p$) and ($m + p$)-**A$_9$** and **F$_8$** from under saturation, respectively. The densities of *op*/*mp*-**A$_9$** and *op*/*mp*-**F$_8$** solutions were determined as $0.9813(x_p = 0.8677)$, $0.9807(x_p = 0.8054)$, $1.1372(x_p = 0.6905)$, $1.1379(x_p = 0.7747)$ g cm^{-1}, respectively. Then the excess enthalpies for the mixtures of ($o + op$) and ($m + mp$)-**A$_9$/F$_8$** were measured with the pure component of *o*-/*m*-isomers as a titrant.

Results and discussion

Experimental measurements were performed over the whole range of the molar fractions for ($o + m$), ($o + p$), ($m + p$)-**A$_2$**, **A$_3$**, **A$_4$**, **A$_6$**, **A$_{10}$**, and ($o + m$)-**A$_9$/F$_8$** are listen in Tables 2, 3 and 4. The observed values were fitted with the Redlich–Kister type equation:

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}
$(1 - x)o$-Ethylmethylbenzene $+ xm$-ethylmethylbenzene							
0.08030	3.522	0.3794	10.49	0.5336	10.85	0.7410	8.181
0.1487	5.857	0.4113	10.83	0.5597	10.63	0.7923	7.059
0.2076	7.493	0.4400	10.97	0.5885	10.50	0.8512	5.523
0.2589	8.636	0.4661	10.98	0.6204	10.22	0.9196	3.314
0.3039	9.582	0.4899	10.94	0.6560	9.800		
0.3438	10.12	0.5098	10.87	0.6959	9.149		
$(1 - x)o$-Tolylacetonitrile $+ xm$-tolylacetonitrile							
0.07812	7.977	0.4040	27.14	0.6068	26.64	0.7476	20.79
0.1449	13.79	0.4327	27.65	0.6276	26.06	0.7979	17.86
0.2027	18.02	0.4545	27.97	0.6463	25.53	0.8556	13.72
0.2531	21.14	0.4937	28.09	0.6633	24.95	0.9222	7.955
0.2976	23.49	0.5277	27.92	0.6786	24.32		
0.3371	25.14	0.5574	27.57	0.6927	23.67		
0.3723	26.36	0.5836	27.16	0.7055	23.01		
$(1 - x)o$-Tolunitrile $+ xm$-tolunitrile							
0.07716	0.8600	0.2993	2.438	0.4713	2.936	0.711	2.52
0.1433	1.412	0.3224	2.519	0.5049	2.969	0.7546	2.278
0.2092	2.016	0.3367	2.579	0.5437	3.000	0.804	1.955
0.2203	2.088	0.3535	2.638	0.5516	3.000	0.8602	1.533
0.2325	2.172	0.3721	2.705	0.5775	2.957	0.9248	0.9110
0.2463	2.226	0.3928	2.738	0.6060	2.909		
0.2617	2.293	0.4159	2.810	0.6373	2.824		
0.2792	2.365	0.4418	2.896	0.6722	2.688		
$(1 - x)o$-Fluorobenzonitrile $+ xm$-fluorobenzonitrile							
0.07277	7.625	0.3857	24.48	0.5812	23.89	0.7625	16.81
0.1357	13.08	0.4139	24.85	0.6018	23.42	0.8106	14.15
0.1906	16.99	0.4352	25.02	0.6204	22.95	0.8653	10.69
0.2389	19.69	0.4720	25.08	0.6374	22.47	0.9278	6.102
0.2818	21.55	0.5043	24.98	0.6529	22.00		
0.3201	22.90	0.5329	24.72	0.6816	20.39		
0.3546	23.85	0.5583	24.32	0.7198	18.84		

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

The coefficients C_i in Eq. 1 and the standard deviations of the fits s_f

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

are listed in Table 6. The results are shown in Fig. 2 together with the enthalpy change for the dimethylbenzene (DMB, $\mathbf{A_1}$) [1, 8], fluoromethylbenzene (FMB, $\mathbf{A_5}$) [1] systems. Enthalpy changes for $(o + m)$-A$_2$ to A$_5$ have been reported previously [1]. The excess enthalpies for binary systems in different solid and liquid state were measured for the first time when the pure components of *o*/*m*-isomers were titrated into the pre-formed *op* or *mp* mixtures for $\mathbf{A_9}$ and $\mathbf{F_8}$ isomers systems. Typically, about 10 injections for each run of experiment are performed using computer-controlled titration. The amount of titrant is about 10–50 µL for each titration. N_L and N_S is the molar number of *o*/*m*- and *p*-isomers in pre-formed solution, respectively. n is the times of titration and ΔN_L is the molar number of injected liquid *o*/*m*-isomers (the amount of change of titrant *o*/*m*-isomers). N_S is constant during one running of experimental titrations, and changed in different running experiments to achieve a large range of molar fraction. The mole fraction of liquid isomers x is shown as Eqs. 3 and 4.

$$x_{n-1} = N_{L,n-1} \big/ \left(N_{L,n-1} + N_{S,n-1}\right) \tag{3}$$

$$x_n = \left(N_{L,n-1} + \Delta N_L\right) \big/ \left(N_{L,n-1} + N_{S,n-1} + \Delta N_L\right) \tag{4}$$

Table 3 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}
$(1 - x)o$-Ethylmethylbenzene + xp-ethylmethylbenzene							
0.07982	0.09672	0.3778	0.7418	0.5219	0.8021	0.7318	0.6034
0.1479	0.2822	0.4097	0.7772	0.5481	0.7863	0.7844	0.5524
0.2065	0.4627	0.4384	0.7994	0.5771	0.7607	0.8452	0.4769
0.2576	0.5521	0.4645	0.8021	0.6093	0.7273	0.9161	0.3302
0.3025	0.6381	0.4763	0.7985	0.6453	0.6888		
0.3423	0.6976	0.4981	0.8065	0.6858	0.6473		
$(1 - x)o$-Diethylbenzene + xp-diethylbenzene							
0.07809	−0.3828	0.3754	−1.092	0.5471	−1.403	0.7073	−1.427
0.1449	−0.6308	0.3935	−1.130	0.5654	−1.433	0.7381	−1.365
0.2026	−0.7927	0.4135	−1.166	0.5850	−1.458	0.7718	−1.273
0.2531	−0.8985	0.4357	−1.210	0.6059	−1.476	0.8087	−1.141
0.2975	−0.9672	0.4604	−1.254	0.6284	−1.485	0.8493	−0.9616
0.3370	−1.011	0.4880	−1.298	0.6527	−1.482	0.8943	−0.7214
0.3588	−1.059	0.5191	−1.344	0.6789	−1.465	0.9442	−0.4067
$(1 - x)o$-Chloromethylbenzene + xp-chloromethylbenzene							
0.08062	−3.120	0.3804	−10.34	0.5405	−11.18	0.7462	−8.360
0.1492	−5.495	0.4123	−10.66	0.5665	−11.09	0.7968	−7.211
0.2083	−7.182	0.4411	−10.91	0.5952	−10.73	0.8547	−5.483
0.2597	−8.439	0.4672	−11.09	0.6269	−10.43	0.9216	−3.160
0.3048	−9.269	0.4910	−11.22	0.6622	−10.11		
0.3447	−9.886	0.5167	−11.20	0.7017	−9.410		
$(1 - x)o$-Methoxymethylbenzene + xp-methoxymethylbenzene							
0.07867	−5.288	0.3741	−15.91	0.5424	−16.62	0.7477	−12.50
0.1459	−8.915	0.4058	−16.41	0.5684	−16.43	0.7980	−10.44
0.2039	−11.38	0.4345	−16.77	0.597	−16.16	0.8556	−7.841
0.2546	−13.03	0.4606	−16.92	0.6287	−15.68	0.9222	−4.621
0.2992	−14.33	0.4843	−16.97	0.6639	−15.00		
0.3388	−15.29	0.5186	−16.67	0.7033	−13.95		
$(1 - x)o$-Tolylacetonitrile + xp-tolylacetonitrile							
0.07897	8.236	0.3751	27.57	0.5345	29.38	0.7416	23.06
0.1464	14.29	0.4069	28.46	0.5606	29.24	0.7928	19.85
0.2046	18.84	0.4356	29.21	0.5893	28.77	0.8516	15.33
0.2554	22.00	0.4616	29.56	0.6212	28.03	0.9199	8.807
0.3001	24.44	0.4854	29.70	0.6568	26.93		
0.3397	26.21	0.5107	29.41	0.6966	25.32		

Yielding Eqs. 3 to 4, the molar number of titrant liquid *o/m*-isomers ΔN_L for each time is expressed by the molar fraction of the titrant and the molar number of the solid *p*-isomer in pre-solution in Eq. 5.

$$\Delta N_{L,n} = \left(\frac{x_n}{1 - x_n}\right) N_{S,n-1} - N_{L,n-1} = \left[\left(\frac{x_n}{1 - x_n}\right) - \left(\frac{x_{n-1}}{1 - x_{n-1}}\right)\right] N_{S,n-1} \quad (5)$$

The heat q observed upon re-equilibration of the system after mixing the titrant and the content in the cell is the enthalpy difference between the previous and the new equilibrium state. Q_{obs-L} is the observed heat per molar of injected liquid, $Q_{obs-L} = q/\Delta n_L$, since $\Delta n_S = 0$ for each run of the experiment in our case, therefore $Q_{obs-L} = h_L$, h_L is the liquid component's excess partial enthalpy. The excess enthalpy can be calculated as Eq. 6. The partial excess enthalpies of the liquid component (Eq. 7) can be calculated as the derivation of Eq. 6 based on the Gibbs–Duhem equation. Considering the polynomial form of excess enthalpy with Eq. 8, and the yield with Eq. 7, the observed heat per mole of liquid injected Q_{obs-L} becomes

Table 4 Excess enthalpies of $(1 - x)m$-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}
$(1 - x)m$-Ethylmethylbenzene + xp-ethylmethylbenzene							
0.07775	−1.496	0.3711	−4.537	0.5363	−4.541	0.7431	−3.487
0.1443	−2.493	0.4028	−4.665	0.5624	−4.503	0.7941	−2.936
0.2019	−3.191	0.4314	−4.736	0.5912	−4.419	0.8526	−2.222
0.2522	−3.697	0.4574	−4.756	0.6230	−4.313	0.9204	−1.258
0.2965	−4.070	0.4812	−4.732	0.6585	−4.131		
0.3359	−4.343	0.5029	−4.666	0.6982	−3.969		
$(1 - x)m$-Diethylbenzene + xp-diethylbenzene							
0.07906	0.8958	0.3754	3.244	0.5307	3.759	0.7387	3.257
0.1465	1.510	0.4072	3.397	0.5569	3.777	0.7903	2.841
0.2048	2.033	0.4359	3.509	0.5857	3.777	0.8497	2.303
0.2556	2.542	0.4619	3.610	0.6177	3.728	0.9188	1.356
0.3003	2.805	0.4857	3.639	0.6534	3.711		
0.3400	3.059	0.5069	3.714	0.6934	3.541		
$(1 - x)m$-Chloromethylbenzene + xp-chloromethylbenzene							
0.07939	−1.683	0.3764	−5.908	0.5181	−6.312	0.7029	−5.264
0.1471	−2.947	0.4082	−6.114	0.5419	−6.288	0.7473	−4.715
0.2055	−3.900	0.4370	−6.252	0.5679	−6.217	0.7977	−4.055
0.2565	−4.610	0.4630	−6.339	0.5965	−6.086	0.8554	−2.983
0.3013	−5.187	0.4868	−6.377	0.6282	−5.894	0.9221	−1.736
$(1 - x)m$-Methoxymethylbenzene + xp-methoxymethylbenzene							
0.08000	−0.5161	0.3784	−1.319	0.5370	−1.397	0.7184	−1.214
0.1482	−0.7825	0.4103	−1.345	0.5606	−1.396	0.7613	−1.088
0.2069	−0.9694	0.4390	−1.358	0.5864	−1.396	0.8096	−0.9447
0.2581	−1.135	0.4651	−1.360	0.6146	−1.368	0.8645	−0.7069
0.3030	−1.224	0.4889	−1.353	0.6457	−1.334	0.9273	−0.4141
0.3429	−1.273	0.5153	−1.366	0.6801	−1.291		
$(1 - x)m$-Tolylacetonitrile + xp-tolylacetonitrile							
0.1561	1.124	0.3303	2.005	0.4789	2.472	0.6604	2.534
0.1875	1.307	0.3483	2.077	0.5177	2.535	0.7000	2.442
0.2347	1.552	0.3684	2.153	0.5385	2.577	0.7447	2.279
0.2859	1.817	0.3909	2.233	0.5645	2.604	0.7955	2.040
0.2993	1.875	0.4164	2.314	0.5932	2.608	0.8537	1.613
0.3140	1.938	0.4455	2.395	0.6250	2.594	0.9211	1.008

Eq. 9. Replacing $\Delta N_{\mathrm{L,n}}$with Eq. 5, the coefficients of f_0, f_1, f_2 are calculated by solving a series of linear equations from Eq. 10 based on least-squares analyses according to the observed $Q_{\mathrm{obs-L}}$.

$$h^{\mathrm{E}} = x_{\mathrm{L}} h_{\mathrm{L}} + x_{\mathrm{S}} h_{\mathrm{S}} \tag{6}$$

$$h_{\mathrm{L}} = h^{\mathrm{E}} + (1 - x_{\mathrm{L}})\left(\partial h^{\mathrm{E}}/\partial x_{\mathrm{L}}\right)_{\mathrm{T,P}} \tag{7}$$

$$h^{\mathrm{E}} = x(1 - x)\left(f_0 + f_1 x + f_2 x^2 + f_3 x^3 + \ldots\right) \tag{8}$$

$$Q_{\mathrm{obs-L}} = q_n/\Delta N_{\mathrm{L},n} = h_{\mathrm{L},n} = (1 - x_n)^2\left(f_0 + 2f_1 x_n + 3f_2 x_n^2\right) \tag{9}$$

$$\frac{q_n}{N_{\mathrm{solid}}} = \left[\frac{x_n}{1 - x_n} - \frac{x_{n-1}}{1 - x_{n-1}}\right](1 - x_n)^2\left(f_0 + 2f_1 x_n + 3f_2 x_n^2\right) \tag{10}$$

The mole fraction of the liquid isomer component x and the heat change of each titration q at different runs of experiments are shown in Tables 5 and 6. The excess enthalpies fitted from Eq. 10 for the *op*/*mp*-mixtures of $\mathbf{A_9}$ and $\mathbf{F_8}$ are also shown in Fig. 2, and the parameters correlated with Eq. 10 are shown in Table 7.

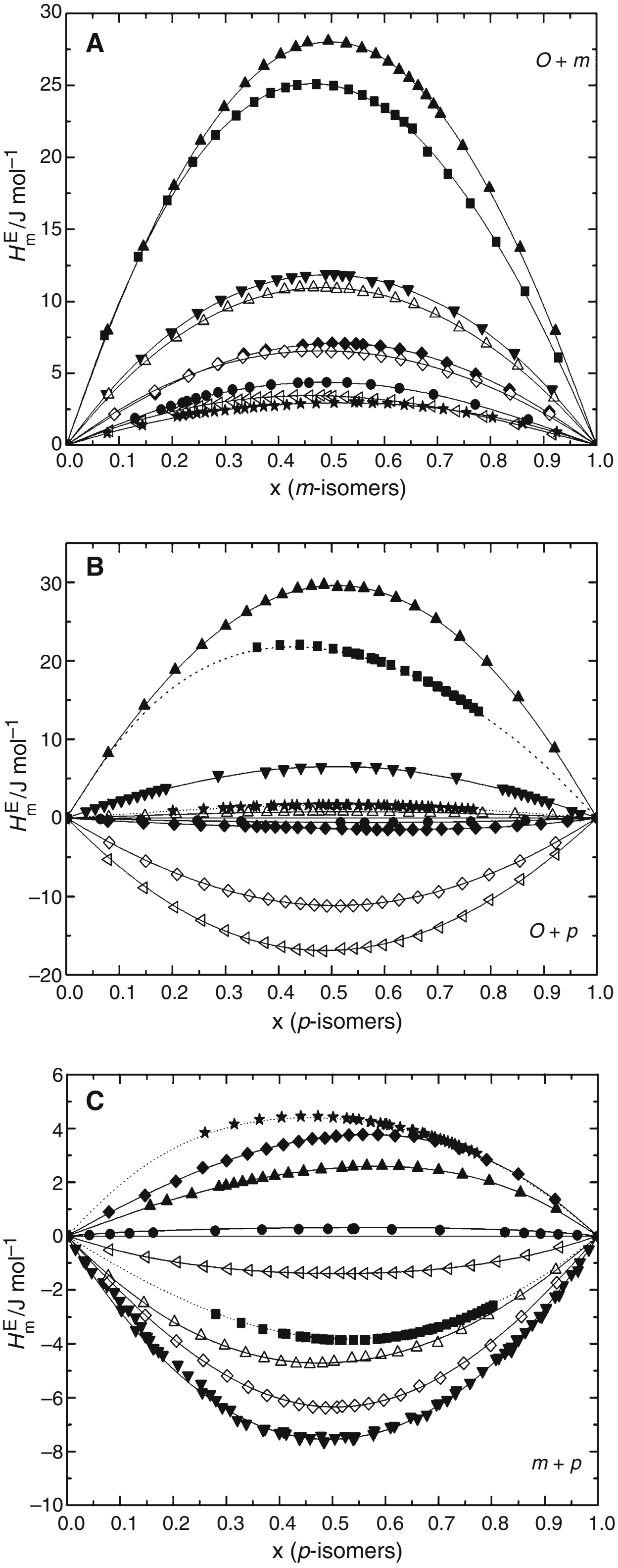

Fig. 2 Excess enthalpies for *o*-, *m*- and *p*-isomers: **A** *o*- + *m*-isomers, **B** *o*- + *p*-isomers, **C** *m*- + *p*-isomers. ▼ $\mathbf{A_1}$,◁ $\mathbf{A_2}$, △ $\mathbf{A_3}$, ◆ $\mathbf{A_4}$, ○ $\mathbf{A_5}$, ◇ $\mathbf{A_6}$, ★ $\mathbf{A_9}$, ▲ $\mathbf{A_{10}}$, ■ $\mathbf{F_8}$

To confirm the determination procedure for the method, the same procedure was applied for the excess enthalpies for ($o + p$)-dimethylbenznene, which contained binary mixtures of two pure liquids. The results showed good agreement with the experimental results. The average standard deviation was 0.25 J mol^{-1} for the fitted and measured results.

All the isomers $\mathbf{A_1}$–$\mathbf{A_6}$ and $\mathbf{A_9}$, $\mathbf{A_{10}}$ are contained in an aliphatic group. The excess enthalpies of ($o + m$)-isomers for all these methyl-substituted groups are positive, the values decrease in the sequence of maximum to minimum: CCNMB ($\mathbf{A_{10}}$) > DMB ($\mathbf{A_1}$) > EMB ($\mathbf{A_3}$) > DEB ($\mathbf{A_4}$) > CMB ($\mathbf{A_6}$) > FMB ($\mathbf{A_5}$) > MOMB ($\mathbf{A_2}$) > CNMB ($\mathbf{A_9}$). Half of the systems are positive, and negative enthalpies for ($o + p$) and ($m + p$)-isomers are shown in Fig. 2 B and C, respectively. The enthalpy changes follow in these sequences, respectively: CCNMB ($\mathbf{A_{10}}$) > DMB ($\mathbf{A_1}$) > CNMB ($\mathbf{A_9}$) > EMB ($\mathbf{A_3}$) > FMB ($\mathbf{A_5}$) > DEB ($\mathbf{A_4}$) > CMB ($\mathbf{A_6}$) > MOMB ($\mathbf{A_2}$), and CNMB ($\mathbf{A_9}$) > DEB ($\mathbf{A_4}$) > CCNMB ($\mathbf{A_{10}}$) > FMB ($\mathbf{A_5}$) > MOMB ($\mathbf{A_2}$) > EMB ($\mathbf{A_3}$) > CMB ($\mathbf{A_6}$) > DMB ($\mathbf{A_1}$). Except for one of the aliphatic-substituted groups on the benzene ring, the other substituted groups are: –CH$_2$–CN, –CH$_3$, –C$_2$H$_5$, –Cl, –F, –OCH$_3$, and –CN, respectively, for all these isomers. The substituted groups of –Cl, –F, –OCH$_3$, –CN are electron-acceptor groups and aliphatic-substituted groups are electron-donor groups. The isomer contains both an electron donor and an electron acceptor group (MOMB ($\mathbf{A_2}$), FMB ($\mathbf{A_5}$), CMB ($\mathbf{A_6}$), CNMB ($\mathbf{A_9}$)) showing less enthalpy change, and it shows the same change as the fluorine-substituted containing isomers, which have been reported in a previous work [2]. Excess enthalpies of CNMB ($\mathbf{A_9}$) showed the most positive results for ($m + p$)-isomers, which might be the effect of the conjugated –CN group. The range of change in enthalpy becomes smaller for these aliphatic-substituted groups containing isomers compared with the fluorine-substituted isomers [2]. The correlations between the excess enthalpy at infinite dilution and the dipole–dipole, dipole-induced dipole, dipole–quadrupole or quadrupole–quadrupole interaction energy of the pair molecules for fluorine-substituted isomers have been studied previously [2]. In this work, the pair intermolecular energy for all the fluorine and alkyl-substituted isomers was calculated using the MP2 (the second-order Moller–Plesset perturbation), with the 6-311G^{++}(d, p) basis set, including the counterpoise correction from the Gaussian method [6]. All energy calculations by the molecular orbital method were performed with the SCF = tight option. The total interaction energies were corrected by Basis Set Superposition Error (BSSE) [6]. The systems containing fluoroiodobenzene were calculated based on the MP2/CEP-121G level of theory from Gaussian 09[23], since the basis set able to handle the large

Table 5 Heat change of each titration for $(1 - x)p$-solid isomer + xm/o-liquid isomer at different runs of experiments at 298.15 K

x	q/mJ	x	q/mJ	x	q/mJ	x	q/mJ
$(o + p)$-Tolunitrile							
$N_{o,1} = 4.218$ mmol^{a}		$N_{o,2} = 9.261$ mmol^{b}		$N_{o,3} = 0.6561$ mmol^{c}		$N_{o,4} = 2.652$ mmol^{d}	
$N_{p,1} = 12.08$ mmol^{a}		$N_{p,2} = 8.288$ mmol^{b}		$N_{p,3} = 4.304$ mmol^{c}		$N_{p,4} = 2.344$ mmol^{d}	
0.2953^{a}	3.4615	0.5494^{b}	1.5912	0.2584^{c}	1.6344	0.5986^{d}	0.2042
0.3284^{a}	3.3938	0.5692^{b}	1.4191	0.3087^{c}	1.4634	0.6257^{d}	0.1936
0.3584^{a}	3.1785	0.5873^{b}	1.3734	0.3525^{c}	1.3039	0.6493^{d}	0.1828
0.3860^{a}	2.5756	0.6039^{b}	1.1740	0.3912^{c}	1.1554	0.6701^{d}	0.1721
0.4112^{a}	2.4487	0.6193^{b}	1.1408	0.4255^{c}	1.0174	0.6886^{d}	0.1616
0.4345^{a}	2.1629	0.6335^{b}	1.0977	0.4561^{c}	0.8891	0.7051^{d}	0.1515
0.4560^{a}	2.0037	0.6466^{b}	0.9601	0.4836^{c}	0.7699	0.7200^{d}	0.1418
0.4759^{a}	1.8479	0.6589^{b}	0.9048	0.5085^{c}	0.6589	0.7334^{d}	0.1325
0.4944^{a}	1.6396	0.6704^{b}	0.7600	0.5311^{c}	0.5554	0.7456^{d}	0.1237
0.5116^{a}	1.5744	0.6811^{b}	0.7211	0.5517^{c}	0.4587	0.7568^{d}	0.1153
0.5277^{a}	1.4447	0.2003^{c}	1.8164	0.5674^{d}	0.2140	0.7670^{d}	0.1074
$(m + p)$-Tolunitrile							
$N_{m,1} = 0.9299$ mmol^{a}			$N_{m,2} = 2.830$ mmol^{b}		$N_{m,2} = 2.442$ mmol^{c}		
$N_{p,1} = 3.848$ mmol^{a}			$N_{p,2} = 2.209$ mmol^{b}		$N_{p,2} = 2.447$ mmol^{c}		
0.2596^{a}	3.6338	0.5711^{a}	0.9550	0.7248^{b}	0.6437	0.6497^{c}	0.9171
0.3149^{a}	3.1051	0.5902^{a}	0.9562	0.7385^{b}	0.6367	0.6695^{c}	0.7814
0.3625^{a}	2.7378	0.6077^{a}	0.6783	0.7508^{b}	0.6359	0.6873^{c}	0.6519
0.4039^{a}	2.2851	0.5992^{b}	1.0919	0.7621^{b}	0.6288	0.7032^{c}	0.6457
0.4403^{a}	1.8878	0.6275^{b}	0.8192	0.7724^{b}	0.5994	0.7175^{c}	0.5461
0.4724^{a}	1.8921	0.6521^{b}	0.8193	0.5390^{c}	1.4336	0.7306^{c}	0.4289
0.5011^{a}	1.6097	0.6737^{b}	0.7756	0.5728^{c}	1.4153		
0.5268^{a}	1.2350	0.6927^{b}	0.6892	0.6019^{c}	1.0856		
0.5500^{a}	1.2335	0.7096^{b}	0.7906	0.6273^{c}	0.9433		
$(o + p)$-Fluorobenzonitrile							
$N_{o,1} = 1.859$ mmol^{a}			$N_{o,2} = 3.841$ mmol^{b}		$N_{o,3} = 2.544$ mmol^{c}		
$N_{p,1} = 4.148$ mmol^{a}			$N_{p,2} = 2.436$ mmol^{b}		$N_{p,3} = 2.505$ mmol^{c}		
0.3594^{a}	13.3198	0.5941^{a}	4.2972	0.7450^{b}	1.9347	0.6610^{c}	3.3270
0.4026^{a}	11.6481	0.6119^{a}	4.0141	0.7569^{b}	1.7487	0.6812^{c}	2.9103
0.4403^{a}	9.7362	0.6388^{b}	3.8070	0.7677^{b}	1.3572	0.6991^{c}	3.0425
0.4735^{a}	8.4673	0.6623^{b}	3.7373	0.7777^{b}	1.3521	0.7151^{c}	2.3601
0.5030^{a}	7.3682	0.6828^{b}	3.4074	0.5459^{c}	5.5497	0.7295^{c}	2.3111
0.5294^{a}	6.4488	0.7011^{b}	2.9955	0.5814^{c}	5.0321	0.7425^{c}	2.1168
0.5532^{a}	5.6631	0.7173^{b}	2.6078	0.6118^{c}	4.5401		
0.5746^{a}	4.9624	0.7319^{b}	2.3124	0.6380^{c}	3.9221		
$(m + p)$-Fluorobenzonitrile							
$N_{m,1} = 4.684$ mmol^{a}		$N_{m,2} = 12.57$ mmol^{b}		$N_{m,3} = 1.390$ mmol^{c}		$N_{m,4} = 3.386$ mmol^{d}	
$N_{p,1} = 8.003$ mmol^{a}		$N_{p,2} = 5.368$ mmol^{b}		$N_{p,3} = 4.779$ mmol^{c}		$N_{p,4} = 2.658$ mmol^{d}	
0.4126^{a}	−6.8570	0.6782^{a}	−1.9295	$^{2}0.8034^{b}$	−1.0322	0.6194^{d}	−0.8071
0.4504^{a}	−4.8633	0.6898^{a}	−1.6959	0.2801^{c}	−3.3814	0.6434^{d}	−0.7301
0.4836^{a}	−4.3481	0.7007^{a}	−1.5576	0.3277^{c}	−3.5098	0.6645^{d}	−0.3065
0.5130^{a}	−4.1564	0.7156^{b}	−2.1689	0.3694^{c}	−3.1164	0.6833^{d}	−0.4136
0.5393^{a}	−4.0682	0.7290^{b}	−2.1437	0.4062^{c}	−3.0840	0.7001^{d}	−0.3219
0.5629^{a}	−4.0268	0.7413^{b}	−2.1395	0.4389^{c}	−2.6173	0.7152^{d}	−0.3294
0.5842^{a}	−3.3597	0.7524^{b}	−2.0631	0.4683^{c}	−2.1624	0.7288^{d}	−0.2378

Table 5 continued

x	q/mJ	x	q/mJ	x	q/mJ	x	q/mJ
0.6035[a]	−2.9996	0.7627[b]	−1.8393	0.4947[c]	−1.9603	0.7412[d]	−0.1634
0.6210[a]	−2.9673	0.7721[b]	−1.5362	0.5186[c]	−1.8479	0.7525[d]	−0.1772
0.6371[a]	−2.8696	0.7808[b]	−1.4187	0.5403[c]	−1.7211		
0.6519[a]	−2.4753	0.7889[b]	−1.3751	0.5602[c]	−1.4717		
0.6656[a]	−2.0431	0.7964[b]	−1.2527	0.5919[d]	−1.0489		

a, b, c and d show the number of series of experiments

Table 6 Best fits coefficients C_i of Redlich–Kister type Eq. 1 with standard deviation of the fits s_f

Samples	C_1	C_2	C_3	s_f/J mol^{-1}
Systems of *o*- and *m*-isomers				
Dimethylbenzene[a]	47.48	1.03	7.63	0.15
Ethylmethylbenzene	43.81	2.40	2.07	0.062
Diethylbenzene[a]	28.44	−1.09	−2.18	0.06
Chloromethylbenzene[a]	26.26	1.89	0.76	0.10
Methoxymethylbenzene[a]	13.71	2.46	−1.27	0.02
Tolylacetonitrile	11.23	1.31	−2.99	0.075
Tolunitrile	11.84	−0.66	1.09	0.038
Fluoromethylbenzene[a]	17.56	1.23	−2.51	0.04
Fluorobenzonitrile	100.1	13.93	2.09	0.11
Systems of *o*- and *p*-isomers				
Dimethylbenzene[c]	26.11	−0.50	−2.63	0.097
Ethylmethylbenzene	3.18	−0.37	−0.57	0.041
Diethylbenzene	−5.36	2.49	−1.89	0.046
Chloromethylbenzene	−44.64	1.12	2.16	0.064
Methoxymethylbenzene	−67.53	−3.42	−0.35	0.12
Tolylacetonitrile	118.5	−4.07	−1.71	0.11
Fluoromethylbenzene[b]	−2.25	0.61	−0.15	0.01
Systems of *m*- and *p*-isomers				
Dimethylbenzene[c]	−30.21	−0.89	0.44	0.090
Ethylmethylbenzene	−18.82	−1.70	−0.45	0.052
Diethylbenzene	14.84	−4.02	0.60	0.028
Chloromethylbenzene	−25.39	0.57	2.94	0.033
Methoxymethylbenzene	−5.57	0.12	−1.38	0.024
Tolylacetonitrile	10.10	−3.29	1.04	0.018
Fluoromethylbenzene[b]	1.26	−0.19	0.61	0.54

a, b and c were cited from references [1, 2, 8], respectively

Table 7 Best fits coefficients f_i of Eq. 10 with standard deviation of the fits s_f

(Liquid + solid)-isomers	f_0	f_1	f_2	s_f/J mol^{-1}
Systems of *o*- and *p*-isomers				
Tolunitrile	4.06	9.97	−9.34	0.039
Fluorobenzonitrile	126.35	−112.98	65.87	0.087
Systems of *m*- and *p*-isomers				
Tolunitrile	24.72	−22.74	17.31	0.046
Fluorobenzonitrile	−12.61	−7.12	3.06	0.13

iodine atom was suggested to be sufficiently extended. The excess enthalpies at $x = 0.5$ $H^{E}_{0.5}$ and the intermolecular energy (*IE*) by the supermolecule method [24] were compared to determine the interaction of the structure isomers.

Two groups are considerably defined based on the two kinds of substituted groups on the benzene ring-fluorine and the aliphatic group. The first group is the fluorine-substituted group containing $\mathbf{F_1}$ to $\mathbf{F_6}$, $\mathbf{F_8}$ and including $\mathbf{A_5}$ (fluoromethylbenzene), which includes both methyl and fluorine, called the **F**-group; The second group is the aliphatic substituted group containing $\mathbf{A_1}$ to $\mathbf{A_6}$, $\mathbf{A_9}$, $\mathbf{A_{10}}$ and $\mathbf{F_7}$ (fluoronitrobenzene contain the fluorine-substituted group, but show the same properties as the aliphatic-containing isomers according to the correlations), called the **A**-group. The correlation between the intermolecular energy and the excess enthalpies at a molar fraction of $x = 0.5$ for all the systems is expressed by Eq. 11, and shown in Fig. 3.

$$H^{E}_{0.5} = a + bIE \tag{11}$$

Here the coefficients a, b are shown in Table 8. Three extra points were partially out of these linear correlations: $\mathbf{F_6}$ in the **F**-group of $(o + m)$-isomers; $\mathbf{A_{10}}$ in the **A**-group of $(o + p)$-isomers; $\mathbf{F_3}$ in the **F**-group of $(m + p)$-isomers.

In all correlations for *o*- and *m*-isomers, *o*- and *p*-isomers, and *m*- and *p*-isomers, interaction energies containing iodine-substituted groups were dissimilar, which might be an effect of basis set difference. The intermolecular energies of the systems containing aminofluorobenzene were considerably smaller.

The effect of the intermolecular energy on the change in excess enthalpy differs considerably based on these two different substituted groups of the benzene ring-fluorine and the aliphatic one. The slope for the **A**-group was close

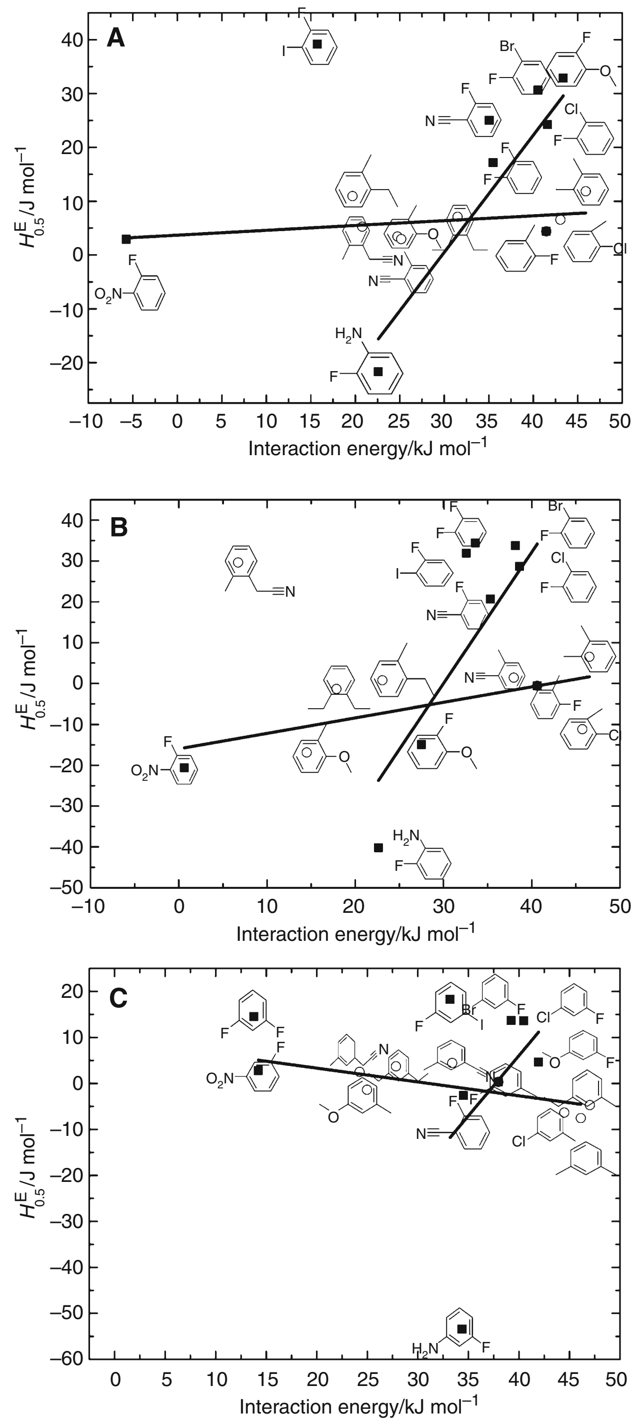

Fig. 3 Correlations between excess enthalpies $H^E_{0.5}$ at equal molar solution and the intermolecular interaction between two isomers: **A** *o*- and *m*-isomers, **B** *o*- and *p*-isomers, and **C** *m*-and *p*-isomers: ■ F-substituted isomers, ○ A-substituted isomers, ◘ fluoromethylbenzene

Table 8 The best fit coefficients by Eq. 11

Systems	A-group			F-group		
	a	*b*	s_f	*a*	*b*	s_f
$(o + m)$-isomers	3.69	0.09	2.83	−64.70	2.17	10.36
$(o + p)$-isomers	−15.96	0.38	6.90	−96.58	3.21	18.28
$(m + p)$-isomers	9.36	−0.30	2.79	−98.70	2.62	21.09

s_f in J mol^{-1}

to zero, however that of the **F**-group was positive and large. This means the effect for the compounds containing aliphatic-substituted groups was smaller than that containing fluorine-substituted isomers, with the increase of the intermolecular energy, the enthalpy change becomes large, which might be a result of the strong electronegative effect of fluorine on the benzene ring.

The subject of intermolecular force is difficult, however, it may consist of the following type of intermolecular forces: London dispersion force, Repulsion forces, Columbic forces, forces between permanent dipoles, forces between ion and permanent dipole, forces between ion and induced dipoles, forces between permanent dipoles and induced dipole, charge-transfer forces, hydrogen bonding, and so forth. In this work, energies due to the dispersion force between each two isomers for *o/m*-, *o/p*- and *m/p*-isomers, dipole-induced dipole moment, and permanent dipole were calculated by Sinoda [25] and Israelachvili [26] according to the previous method. The dipole moment and polarizability of *o*-, *m*- *p*-isomers have been calculated from Gaussian [6, 24]. The energies due to dipole-induced dipole moment and the dispersion force between two isomers for *o/m*-, *o/p*- and *m/p*-isomers did not show a clear correlation between those energies and the excess enthalpies observed. The energies due to dipole–dipole interaction (Keesom energy) u_{12}:

$$u_{12} = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)^2 r^6 kT} \propto \frac{\mu_1^2\mu_2^2}{(r_1 + r_2)^6} \qquad (12)$$

and the excess enthalpies at the molar fraction of $x = 0.5$ are shown in Fig. 4. Here μ, r, and k are dipole moment, the 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 $(r_1 + r_2)$. Here r_1 and r_2 was the molecular radius of *o*-, *m*-, and *p*-isomers calculated from the densities in the first column of Table 1, respectively.

Although the Keesom energies [27] were not so large, large stabilization by the Keesom energy showed smaller excess enthalpies to negative excess enthalpies for the A-group isomers. Also, the difference of dipole moment is larger, and the range of enthalpy change is large from negative to positive for the F-group isomers. This means that the effect of dipole moments on enthalpic stabilization plays no small part in the interaction between isomers.

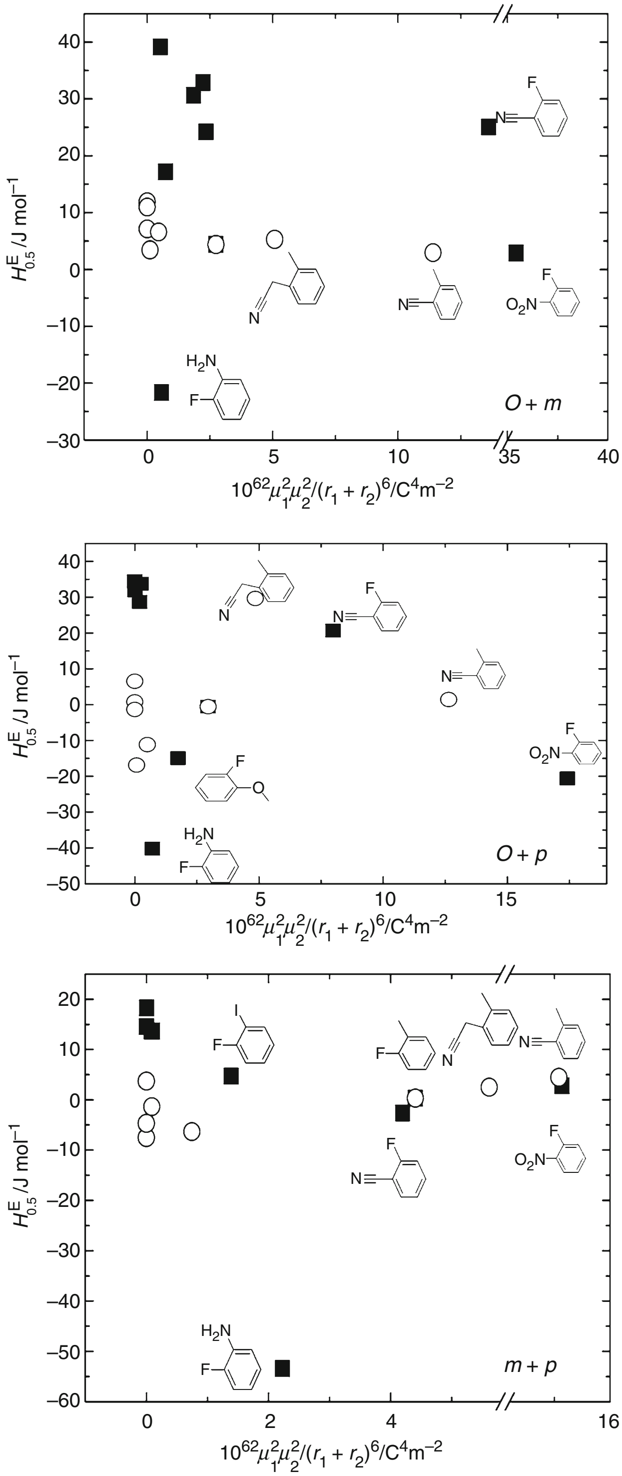

Fig. 4 Correlations between excess enthalpies$H^E_{0.5}$ at equal molar solution and the Keesom energies of the two isomers: *open circle* A-group, *filled square* F-group

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