

Excess Enthalpies for Binary Mixtures of *o*-Xylene + *o*-Disubstituted Isomers

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The excess enthalpies for binary mixtures of *o*-xylene+ *o*-disubstituted isomers (ethyltoluene, methoxytoluene, fluorotoluene, chlorotoluene, bromotoluene, iodotoluene, tolylacetonitrile, fluoroiodobenzene, bromofluorobenzene, chlorofluorobenzene, fluoronitrobenzene, amino-fluorobenzene) were measured at 298.15 K. The excess enthalpies are small for these binary systems except systems of (xylene + fluoronitrobenzene) and (xylene + aminofluorobenzene), which show larger positive excess enthalpies. The experimental results were compared according to the group contribution method UNIFAC (Dortmund), regular solution theory and COSMO-RS of DFT. UNIFAC predictions were positive and differed significantly from the observed results. However, excess enthalpies calculated by the COSMO-RS model showed better agreement than the others. There was a correlation between excess enthalpies and dipole-dipole interaction energy by the Keesom-Israelachvili equation.

Keywords: Excess enthalpies, o-disubstituted isomers, intermolecular energy, UNIFAC, COSMO-RS.

1. Introduction

The small excess enthalpies based on the small difference of the molecular structure, such as isotopic molecules,^{1,2)} enantiomer molecules,³⁻¹⁰⁾ and structure isomers¹¹⁻¹⁴⁾ have been investigated. For these simple o-, m- and p-isomers molecules, the different position and kinds of substitute can result in different electronic properties on the π -electron of the benzene ring and different intermolecular interactions in the mixed solution, and cause different excess enthalpies for binary mixtures of these isomers. We are interested in the correlation of the excess enthalpies based on the small differences of the structures of isomers. In our previous studies, the excess enthalpies for 18 binary mixtures of (o + m), (o+p), (m+p)-isomers were measured and discussed^{13,14)}. To clarify the interaction of the substitution effect of o-isomers, the excess enthalpies for 12 binary mixtures of (o-xylene + o-disubstituted isomers) were measured.

The binary mixtures of o-xylene and o-disubstituted

isomers are predicted by means of the UNIFAC, regular solution and conductor-like screening model for realistic solvents method (COSMO-RS), and compared with values of experimental data.

2. Experimental

o-Xylene(xylene), *o*-ethyltoluene(1), *o*-methoxytoluene(2), *o*-fluorotoluene(3), *o*-chlorotoluene(4), *o*bromotoluene(5), *o*-iodotoluene(6), *o*-tolylacetonitrile(7), *o*-fluoroiodobenzene(8), *o*-bromofluorobenzene(9), *o*chlorofluorobenzene(10), *o*-fluoronitrobenzene(11), and *o*-aminofluorobenzene(12) (Tokyo Chemical Industry) were purified and kept with freshly activated molecular sieves 4 A which evacuated at 498 K for more than 4 h under 10^{-2} to 10^{-3} Pa to remove all traces of moisture. The results of purity analysis by the GLC (Simadzu, GC-2014) were more than 99.9 %. Water contents with the coulometric Karl-Fischer's method (Mitsubishi Chemical Moisture Meter CA-02) were less than 0.002 mole%. The excess enthalpies were measured by heat-conduction

o-isomers	ρ	$\Delta_{ m v} H^{ m a}$	$\mu^{ m b}$	r ^b
	/ g ml $^{-1}$	/kJ mol ⁻¹	/ D	$/10^{-10}$ m
o-xylene	0.87596	36.24	0.58	4.67
1	0.87772	38.41	0.65	4.84
2	0.97492	39.07	1.31	4.77
3	0.99850	33.99	1.58	4.52
4	1.0770	37.67	1.86	4.65
5	1.4180	39.99	1.85	4.71
6	1.7176	42.95	1.80	4.78
7	1.0062	48.10	4.05	4.85
8	1.9230	40.81	3.55	4.65
9	1.6043	37.23	3.05	4.57
10	1.2344	35.82	3.16	4.49
11	1.3290	44.65	6.00	4.55
12	1.1477	41.87	1.91	4.46

Table 1 Physical properties of o-isomers

 From SciFinder links (Calculated using Advanced Chemistry Development (ACD/Labs) Software
 V9.04 for Solaris (1994-2010 ACD/Labs)

^b Calculated from Gaussian, Hyperchem and ChemPlus in this work.

microcalorimeter (Thermometric, Thermal Activity Monitor 2277) in the same manner as that described previously.^{2,4,13,14)} Excess enthalpies of (o + m)-xylene at 298.15 K were measured and showed good agreement with the reference.^{2,12)} The densities of the samples were measured using a vibrating-tube densitometry (Anton Paar DMA55) and reported in our previous studies^{13,14)} as shown in **Table 1**.

3. Results and discussion

The excess enthalpies of binary mixtures of (*o*-xylene + *o*-disubstituted isomers) were measured over the whole range of mole fraction and listed in **Table 2** and shown in **Fig.1**. The experimental results were fitted with the Redlich-Kister type equation:

$$H_{\rm m}^{\rm E} = x(1-x)\sum_{i=1}^{3} A_i (1-2x)^{i-1}$$
(1)

The coefficients A_i in eq.(1) and the standard deviations of the fits s_f were

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

shown in **Table 3**. Binary systems of (o-xylene + odisubstituted isomers) show small excess enthalpies the same as the previous (o + m), (o + p), (m + p)-isomers



Fig.1 Excess enthalpies for *o*-xylene+*o*-disubstituted isomers at 298.15 K: *o*-disubstituted isomers; ▲,

1; \blacksquare , 2; \Box , 3; \bigcirc , 4; \triangle , 5, \bigtriangledown , 6; \triangleleft , 7; \checkmark , 8; \triangleleft , 9; \triangleright , 10; \blacklozenge , 11; \bigstar , 12.

systems, except for (xylene + 11) and (xylene + 12). The absolute value of the maximum excess enthalpies in the whole mole fraction for (xylene + 11) and (xylene + 12) was 280.21 and 567.60 J mol⁻¹, respectively, whereas it was no more than 118 J mol⁻¹ for other systems. The reason for the large excess enthalpies for binary systems of (xylene + 11) and (xylene + 12) might be the resonance effect caused by the delocalization of the nitrogen lone pair electronic density on the benzene ring.

Excess enthalpies for (o-xylene + o-disubstituted isomers) systems decreased in the sequence: (xylene + 12) > (xylene + 11) > (xylene + 7) > (xylene + 6) > (xylene + 2) > (xylene + 1) > (xylene + 3) > (xylene + 5) > (xylene + 4) > (xylene + 10) > (xylene + 9) > (xylene + 8). The first five systems show positive excess enthalpies and the others are negative. Binary systems of o-xylene mixed with o-disubstituted isomers containing a substituent of fluorine ((xylene + 10), (xylene + 9), (xylene + 8)) show more negative excess enthalpies and more stabilization than o-disubstituted isomers containing a methyl group except (xylene + 12) and (xylene + 11).

The difference between all *o*-disubstituted isomers structures derives from the difference of the two substituents on the benzene ring in *ortho*-position. The UNIFAC model is applied to clean the contribution of these substituents to the excess enthalpies. The UNIFAC and modified UNIFAC (Dortmund) model¹⁶ is the most

Table 2 Excess enthalpies of xo-xylene + (1-x)o-disubstituted isomers at 298.15 K.

x	$H^{\rm E}$	х	$H^{\rm E}$	х	$H^{\rm E}$	x	HE	<i>x</i>	$H^{\rm E}$	х	$H^{\rm E}$	х	$H^{\rm E}$	x	$H^{\rm E}$
	J mol ⁻¹		J mol ⁻¹		J mol ⁻¹		J mol ⁻¹		J mol ⁻¹		J mol ⁻¹		J mol ⁻¹		J mol ⁻¹
		x	xylene +	+ (1-x)	1					x	xylene +	-(1-x)	8		
0.08546	-1.409	0.3955	-4.797	0.5605	-5.343	0.7372	-4.575	0.07158	-24.89	0.3911	-103.8	0.6466	-118.7	0.9056	-51.22
0.1575	-2.493	0.4278	-4.941	0.5838	-5.310	0.7781	-4.110	0.1336	-45.18	0.4175	-108.0	0.6871	-114.4	0.9201	-44.32
0.2190	-3.293	0.4568	-5.026	0.6092	-5.261	0.8238	-3.460	0.1879	-61.20	0.4477	-111.9	0.7329	-106.8	0.9350	-36.73
0.2721	-3.869	0.4831	-5.045	0.6368	-5.241	0.8752	-2.626	0.2357	-73.39	0.4825	-114.9	0.7854	-94.27	0.9505	-28.53
0.3184	-4.281	0.5069	-5.067	0.6671	-5.127	0.9335	-1.409	0.2782	-82.74	0.5233	-118.6	0.8459	-74.49	0.9664	-19.62
0.3593	-4.562	0.5400	-5.246	0.7004	-4.936			0.3163	-89.64	0.5495	-120.2	0.8648	-69.31	0.9829	-10.05
		r	vvlene -	+ (1 - r)	2			0.3473	-95.05	0.5785	-120.9	0.8779	-63.71	0.9056	-51.22
		л	xyiene	(1 ,)	-			0.3679	-99.48	0.6106	-120.6	0.8916	-57.73		
0.08333	13.01	0.3889	41.24	0.5546	43.05	0.7569	32.39	0.0716	-24.89	0.3911	-103.8	0.6466	-118.7		
0.1538	22.44	0.4210	42.47	0.5805	42.60	0.8059	27.58			x	xylene +	-(1-x)	9		
0.2143	29.10	0.4500	43.26	0.6088	41.80	0.8616	20.84								
0.2667	33.82	0.4762	43.66	0.6401	40.57	0.9257	11.84	0.0683	-19.62	0.354	-76.3	0.5824	-94.24	0.8697	-47.66
0.3125	37.18	0.5000	43.83	0.6/48	38.66			0.1279	-34.89	0.3755	- /9.56	0.6145	-93.46	0.8841	-42.97
0.3329	39.34	0.3310	43.27	0.7155	33.90			0.1805	-40.92	0.3997	-02.03	0.6505	-91.27	0.899	-37.93
		x	xylene +	+ $(1-x)$	3			0.2208	-50.12	0.4273	-88.67	0.0905	-80.77	0.9144	-32.05
0.07008	4 409	0 2495	18.02	0.5216	10.61	0 7216	15 80	0.2005	-68.68	0.4958	-90.87	0.7881	-70.37	0.9468	-20.87
0.1226	-4.498	0.3463	-18.02	0.5210	-19.01	0.7510	-13.69	0.3176	-70.19	0.5274	-93.34	0.8423	-56.21	0.9639	-14.41
0.1320	-11.04	0.3794	-10.79	0.5768	-19.7	0.7842	-10.31	0.3348	-73.21	0.5535	-93.95	0.8558	-52.1	0.9816	-7.414
0.2341	-14 07	0.4331	-19.49	0.6090	-19.27	0.9160	-6.03								
0.2764	-15.72	0.4566	-19.71	0.6451	-18.6	0.9100	0.05			х	xylene +	$(1-x)^{-1}$	10		
0.3143	-17.07	0.4978	-19.50	0.6856	-17.55			0.06709	-18.78	0.3929	-79.05	0.5996	-87.10	0.8748	-40.47
								0.1257	-33.96	0.4076	-81.95	0.6360	-84.98	0.8887	-36.38
		х	xylene +	+ (1-x)	4			0.1775	-46.00	0.4337	-84.13	0.6771	-81.14	0.9031	-32.05
0.07832	-16.37	0.3730	-53.40	0.5445	-57.67	0.7493	-44.51	0.2234	-55.47	0.4634	-85.98	0.7238	-74.74	0.9179	-27.49
0.1453	-28.72	0.4047	-54.92	0.5705	-57.16	0.7994	-38.38	0.2645	-62.93	0.4975	-87.39	0.7775	-64.98	0.9332	-22.59
0.2031	-37.77	0.4334	-55.89	0.5991	-56.23	0.8567	-29.61	0.3014	-68.67	0.5370	-88.05	0.8398	-50.37	0.9491	-17.39
0.2537	-43.72	0.4594	-56.39	0.6307	-54.68	0.9228	-17.38	0.3348	-73.11	0.5380	-88.06	0.8483	-48.07	0.9655	-11.90
0.2982	-48.04	0.4831	-56.67	0.6658	-52.38			0.3652	-76.54	0.5672	-88.04	0.8613	-44.36	0.9824	-6.141
0.3377	-51.13	0.5208	-58.00	0.7051	-49.12					x	xylene +	$(1-x)^{-1}$	1		
		x	xylene +	+ (1- <i>x</i>)	5			0.01396	21.12	0.2635	243.6	0.6192	270.7	0.8459	167.9
0.07382	-8.509	0.3581	-26.76	0.5378	-29.91	0.7243	-26.00	0.02753	40.68	0.3072	259.1	0.6637	259.2	0.8592	158.4
0.1375	-14.61	0.3894	-27.50	0.5677	-30.03	0.7665	-23.59	0.04073	58.61	0.3459	267.6	0.7150	240.4	0.8728	148.1
0.1930	-18.79	0.4177	-28.03	0.5934	-29.77	0.8141	-20.16	0.05358	75.41	0.3580	270.2	0.7263	235.3	0.8869	136.6
0.2417	-22.00	0.4369	-28.75	0.6215	-29.33	0.8678	-15.44	0.06609	90.93	0.3811	274.4	0.7378	229.7	0.9015	124.0
0.2850	-24.15	0.4660	-29.25	0.6523	-28.62	0.9292	-8.950	0.07827	105.4	0.4073	277.2	0.7498	223.8	0.9165	109.9
0.3235	-25.75	0.4993	-29.50	0.6864	-27.54			0.09014	118.7	0.4374	278.1	0.7622	217.4	0.9321	93.99
		r	vvlene -	+ (1 - r)	6			0.1017	131.2	0.4638	275.0	0.7750	210.8	0.9482	75.69
		л	xylene	(1 ,)	0			0.1130	142.7	0.4883	278.2	0.7882	203.8	0.9641	20.22
0.07689	15.51	0.3683	43.12	0.5459	46.77	0.7503	38.49	0.1240	102.6	0.5150	280.1	0.8019	190.1	0.9817	30.32
0.1428	25.01	0.3999	44.35	0.5718	46.78	0.8003	33.50	0.1739	215.0	0.5400	280.0	0.8100	107.0		
0.1999	31.50	0.4285	45.19	0.6004	46.44	0.8574	26.26	0.2140	213.9	0.5805	277.1	0.8507	170.9		
0.2499	36.02	0.4544	45.57	0.6320	45.63	0.9232	15.79			x	xylene +	$(1-x)^{\frac{1}{2}}$	12		
0.2940	39.06	0.4812	46.20	0.6670	44.20			0.06104	120.8	0 2727	502.2	0 6570	5676	0.0078	250.9
0.3332	41.36	0.5222	46.54	0.7062	41.92			0.1167	241.4	0.3727	512.7	0.0370	541.4	0.9078	230.8
		x	xvlene -	+(1-x)	7			0.1107	315.2	0.3977	548.0	0.7615	J41.4 404.5	0.9248	164.2
			· · · · ·	`				0.2089	370.4	0.4892	561.0	0.8311	407.3	0.9610	114.3
0.08714	20.27	0.4621	68.92	0.6587	75.19	0.9129	40.82	0.2482	411.9	0.5156	571.6	0.8454	381.5	0.9801	59.22
0.1603	34.22	0.4884	70.41	0.6897	72.80	0.9244	30.96	0.2838	443.9	0.5449	579.4	0.8602	353.4		
0.2220	44.32	0.5122	72.00	0.7237	70.22	0.9362	32.01	0.3161	468.6	0.5778	582.2	0.8755	322.4		
0.2703	57.10	0.5300	74.14	0.7013	66.00	0.9483	21.84	0.3456	488.0	0.6149	579.4	0.8913	288.3		
0.3642	61.26	0.5708	75.11	0.8029	58 0/	0.900/	15.02								
0.4006	64.44	0.6268	75 53	0.8810	50.25	0.9866	8.634								
0.4330	66.90	0.6304	75.24	0.9016	44.25	0.2000	0.004								
		T													

o-disubstituted	A_1	A_2	A_3	S_f / J mol ⁻¹
isomer				
1	-20.93	4 35	-1 40	0.089
2	174.73	-2.97	-2.19	0.13
3	-80.13	3.57	7.29	0.27
4	-230.26	8.59	-13.32	0.36
5	-119.11	12.18	-20.71	0.32
6	186.69	-13.56	47.18	0.42
7	281.72	-130.03	164.57	1.25
8	-468.73	143.66	-30.38	0.96
9	-367.56	92.21	13.50	1.3
10	-350.72	50.02	24.06	0.76
11	1120.8	50.8	440.4	2.4
12	2269.4	-480.0	639.6	6.5

Table 3 Best fits coefficients A_i of Redlich-KisterEquation with standard deviation S_f for xo-
xylene + (1-x)o-disubstituted isomers

800 12 $H_m^{\rm E}$ / J mol⁻¹ 600 400 7 8 200 i0, 0 0.0 0.2 0.4 0.6 0.8 1.0x(o-xy)

Fig.2 Excess enthalpies from UNIFAC(Dortmund) model for binary systems of o-xylene+odisubstituted isomers at 298.15 K: (xylene + 1 / 2 / 3 / 4 / 5 / 6 / 7 / 8 / 9 / 10 / 11 / 12).

successful predictive model for the excess Gibbs free energy G^E in which a molecule is described as a collection of independent functional groups and a mixture is formed from these functional groups. Recognizing the inability of the UNIFAC model prediction for o - / m - / p-isomers originating from the same functional groups on the benzene ring,¹⁵⁾ the focus of the present study is the effect of different substituents between o-xylene and odisubstituted isomers. Activity coefficients of o-isomers were calculated using the Justemix program (Biosoft,

o-disubstituted isomer	Experime	Calculated	
	$H^{\mathrm{E},\infty}{}_{o}$ -xylene	$H^{\mathrm{E},\infty}{}_{o}$ -isomers	E_K
1	-17.98	-26.67	-0.19
2	169.6	175.5	-0.79
3	-69.26	-76.40	-1.34
4	-235.0	-252.2	-1.71
5	-127.7	-152.0	-1.62
6	220.3	247.4	-1.48
7	316.3	576.3	-7.11
8	-355.5	-642.8	-6.23
9	-261.8	-446.3	-4.83
10	-276.6	-376.7	-5.46
11	1612	1510.5	-19.01

Table 4 Limiting excess partial molar enthalpies for xo-xylene + (1-x)o-disubstituted isomers and

calculated Keesom energy in J mol⁻¹.

 $\overline{E_K}$, Keesom energy from eq.7.

2429

12

Cambridge, UK). The excess Gibbs energy can be calculated according to the activity coefficients *r*:

3389

-2.04

$$G^{E} = x_{1}RT\ln r_{1} + x_{2}RT\ln r_{2}$$
(3)

The excess enthalpies of mixing ΔH^{E}_{m} , can be calculated from the excess Gibbs energy according to the Gibbs-Helmholtz equation:

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P} = -\frac{\Delta H}{T^{2}}$$
(4)

The estimated excess enthalpies for (*o*-xylene + *o*-disubstituted isomers) by UNUFAC are shown in **Fig.2**. All excess enthalpies estimated are positive, and some of the results show a reverse label with the negative experimental results. Most of them are small except for the mixing of (xylene + 12) and (xylene + 11), which show large positive excess enthalpies. The predicted results for (xylene + 12) and (xylene + 11) are comparatively close to the experimental results. (280.21 and 567.60 J mol⁻¹ experimental, and 300.97, 889.22 J mol⁻¹ estimated results at equimolar solution, respectively). That means the UNIFAC model was unsuccessful in accounting for the change of one functional group on the benzene ring between these similar *o*-isomers, which has small excess enthalpies, but

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Fig.3 Excess enthalpies from COSMo-RS model for binary systems of o-xylene+o-disubstituted isomers at 298.15 K: (xylene + 1 / 2 / 3 / 4 / 5 / 6 / 7 / 8 / 9 / 10 / 11 / 12).



Fig.4 Excess enthalpies of regular solution theory of o-xylene+o-disubstituted isomers at 298.15 K: xylene + 1 / 2 / 3 / 4 / 5 / 6 / 7 / 8 / 9 / 10 / 11 / 12.

Table 5	Comparison of	excess enthalpie	s of o-xylene+	o-disubstituted	isomers at	equimolar	solution	$H^{E}_{0.5}$ between
tł	ne observed resu	ilts and UNIFAC	, COSMO-RS a	and Regular sol	ution theor	у.		

o-disubstituted isomer	$H^{E}_{0.5}$ (Experiment)	$H^{E}_{0.5}$ (UNIFAC)	$H^{E}_{0.5}$ (COSM-RS)	$H^{E}_{0.5}$ (Reg. Soln.)
1	-5.23	142.2	18.53	9.50
2	43.68	198.5	20.87	4.14
3	-20.03	19.92	-5.96	2.00
4	-57.56	18.68	-12.37	11.12
5	-29.78	74.18	-14.41	25.41
6	46.67	187.7	-14.50	37.69
7	70.43	337.6	215.8	115.4
8	-117.18	306.0	-37.74	67.41
9	-91.89	41.81	-35.73	40.17
10	-87.68	108.7	-36.11	34.93
11	280.21	301.0	191.1	292.7
12	567.60	889.2	159.3	330.4

was in agreement with larger excess enthalpies' systems.

Excess enthalpies calculated by simple regular solution theory¹⁷) according to eq.(5) are also plotted in **Fig.4**.

$$\Delta H^{M} = (x_{1}v_{1} + x_{2}v_{2}) \left[\left(\frac{\Delta_{V}H_{1}}{v_{1}} \right)^{\frac{1}{2}} - \left(\frac{\Delta_{V}H_{2}}{v_{2}} \right)^{\frac{1}{2}} \right]^{2} \Phi_{1}\Phi_{2} \quad (5)$$

Where $\Delta_v H$, x, v, and $\boldsymbol{\Phi}$ are the enthalpies of vaporization, molar fraction, molar volume and volume fraction, respectively. The enthalpies of vaporization by Advanced Chemistry Development Software (V9.04),

are shown in **Table 1** together with the density of the isomers.

Excess enthalpies of binary mixtures of (*o*-xylene + *o*-disubstituted isomers) were also calculated from COSMO-RS^{18,19)} by ADF (Amsterdam Density Functional software) based on the Density Functional Theory. The results from COSMO-RS are shown in **Fig.3**.

At the same time, excess enthalpies at equimolar solution $H_{0.5}^{\rm E}$ from UNIFAC, COSMO-RS and regular solution theory predictions were compared with the experimental results, as listed in **Table 5**. Compared

with the UNIFAC (Dortmund) approximation and regular solution theory prediction, comparatively reliable results were obtained from COSMO-RS method as shown in **Fig.3**. The advantage of the COSMO-RS prediction in this study is the estimated value showing the same sign of positive and negative excess enthalpies with the experimental results, except for (xylene + 1) and (xylene + 6), which show reverse sign with experimental results. However, the COSMO-RS predictions of the mixtures were smaller absolute values of H_m^E compared with the experimental results, except for (xylene + 7).

The macroscopic properties of excess enthalpies are based on the microscopic intermolecular interaction, to clear the effect of the intermolecular interaction on the excess enthalpies, the intermolecular interaction energy was computed by the Gaussian method^{20,21} using the MP2/6-311⁺⁺G(d,p) basis set in solvents. After the molecular geometry optimization, the total interaction energies (IE) were corrected by Basis Set Superposition Error (BSSE).²¹⁾ Correlations between the *IE* and the excess enthalpies at equimolar solution are shown in Fig.5. Two main relationships were found except (xylene + 12) and (xylene + 11) systems, which showed irregular large excess enthalpies. Firstly, correlations for binary systems of (xylene + 1 / 2 / 3 / 4 / 5 / 6 / 7), secondly, (xylene + 8 / 9 / 10) binary systems. These correlations were fitted with eq.(6).

$$H_{0.5}^E = a + bIE \tag{6}$$

Fitted coefficients from eq.(6) are shown in **Table 6**. For the first relationship in which all the isomers contain a methyl group on the benzene ring, with the increase of the intermolecular interaction energy, excess enthalpies decrease, and the mixtures become more stable, which is contrary to the second relationship.

In order to clarify the major interaction of mixtures, the pair-molecular potential energy of dipole-dipole, dipole-induced dipole and dispersion interaction²²⁾ between o-xylene and o-disubstituted isomer were measured. The dipole moments, polarizabilities and other physical properties of o-disubstituted isomers were calculated using a Gaussian program, HyperChem and ChemPlus.^{23,24)} The calculated dipole moments are shown in **Table 1**, and the pair-molecular Keesom energies (dipole-dipole interaction energy) were calculated from the Keesom-Israelachvili equation^{22,25)} listed in **Table 4**:

Table 6 Best fits coefficients of eq. 6 and 8.

Eq.6	$H^{\rm E}_{0.5} = a + bIE$		eq.8 H^{∞}_{inf}	$H^{\infty}_{inf inite} = \alpha + \beta E$		
	a	b		α	β	
First	356.9	-7.70	$H^{\mathrm{E},\infty}{}_{o}$ -xylene	73.1	68.2	
Second	-635.6	13.0	$H^{\mathrm{E},\infty}{}_{o}\text{-isomers}$	118.2	110.6	



Fig.5 Correlation between excess enthalpies at equimolar solution $H_{0.5}^{E}$ and intermolecular interaction for: \bigcirc , xylene +1 / 2 / 3 / 4 / 5 / 6 / 7; \triangle , xylene + 8 / 9 / 10 / 11 / 12. Dotted line, $H_{0.5}^{E} =$ -635.6 + 13.0*IE*; solid line, $H_{0.5}^{E} =$ -356.9 + 7.70*IE*.





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$$E_{K} = -\frac{2\mu_{1}^{2}\mu_{2}^{2}}{3(4\pi\varepsilon_{0})^{2}k_{B}Tr^{6}} \cdot N_{A}$$
(7)

Where, μ , molecular dipole moment; k_B , Boltzmann constant; T, temperature; r, interaction distance between the centres of two molecules; N_A , Avogadro' number. rwas calculated using HyperChem and ChemPlus QSAR programs²³⁾ after geometry optimization of the molecules. The dipole-induced dipole and dispersion interaction between the measured *o*-xylene and *o*-isomer found no significant correlation. However, the correlations between the partial excess enthalpies at infinite solution and the Keesom energy are shown in **Fig.6** for the binary isomers systems except (xylene + **7** / **12** / **11** MCCNB / FAB / FNB). Some linear correlations were fitted with eq.(8), and the coefficients are shown in **Table 6**:

$$H_{\inf inf inite}^{\infty} = \alpha + \beta E_K \tag{8}$$

The partial molar excess enthalpies decreased with increasing the dipole-dipole interaction energy, and the binary systems became more stable. The major interaction for the binary system of o-xylene+o-disubstituted isomers might be the pair molecular interaction between dipole and dipole molecules.

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Excess Enthalpies for Binary Mixtures of o-Xylene + o-Disubstituted Isomers



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