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Excess enthalpies of some halogenized aromatic compounds + methyl methylthiomethyl sulfoxide or + dimethyl sulfoxide at 298.15 K

XI. Thermodynamics of liquid mixtures containing methyl methylthiomethyl sulfoxide[1]

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Abstract

Excess enthalpies of binary mixtures between each of chlorobenzene, fluorobenzene, bromobenzene, chlorotoluene and fluorotoluene and methyl methylthiomethyl sulfoxide (MMTSO) or dimethyl sulfoxide (DMSO) have been determined at 298.15 K. All mixtures showed positive enthalpy change over the whole range of mole fractions. Partial molar enthalpies of the mixtures containing MMTSO(2) around 0.95 in mole fraction have maxima and minima. Linear relations are obtained between limiting excess partial molar enthalpies and the square of the dipole moment except $H_2^{E,\infty}$ of the mixtures containing fluorotoluene.

Keywords: Enthalpy; Halogenized aromatic compounds

1. Introduction

In our previous papers [1–8], excess thermodynamic functions for the binary mixtures of methyl methylthiomethyl sulfoxide (MMTSO) with water, benzene, dimethyl sulfoxide (DMSO), carbon tetrachloride, chloroform, dichloromethane, deuterochloroform, n-alkane-1-ols(n-$C_nH_{2n+1}OH$, n = 1–9), six methyl-benzenes ($C_6H_{6-n}(CH_3)_n$, n = 1–3), six cycloethers (1,3- and 1,4-dioxanes, oxane, oxolane, 1,3-dioxolane and oxepane), three

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alkyl ethers (diethyl ether, ethylpropyl ether and dipropyl ether) and those of DMSO were reported.

In order to obtain further information on the thermodynamic properties of the mixtures and the molecular structures of their components, particularly to compare the correlations with those of mixtures of methylbenzenes, excess enthalpies of the mixtures between MMTSO and some halogenized aromatic compounds (chlorobenzene, fluorobenzene, bromobenzene, chlorotoluene and fluorotoluene) were determined over the whole range of mole fractions. Those of halogenized aromatic compounds + DMSO were also determined as the reference systems.

2. Experimental

2.1. Materials

Procedures of purification and the final purities of MMTSO (Nippon Soda Co.) and DMSO (Merck, uvasol) were the same as those described previously [1,2]. Chlorobenzene, fluorobenzene, bromobenzene, chlorotoluene and fluorotoluene (Kishida, GR) were fractionally distilled over P_2O_5 or freshly activated molecular sieves 4A which had been evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa. GLC results obtained by using each 2-m column of 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with FID on Yanagimoto G180FP showed merely some trace impurity peaks ($<10^{-7}$). Coulometric Karl-Fischer's method on a Moisturemeter (Mitsubishi Chemical Ind., CA-02) gave the water content of each sample to be 0.01 mol% or less.

2.2. Apparatus and procedures

A twin-microcalorimeter of heat-conduction type (laboratory designation MC-AII) was used for measurements of excess enthalpies at 298.15 K over the whole range of mole fraction. The details of the calorimetric procedures and the reproducibility test of this calorimeter system have been described elsewhere [2,4,9].

3. Results and discussion

The experimental results of excess enthalpies obtained are summarized in Table 1 and plotted in Figs. 1 and 2. All the excess enthalpies observed were positive over the whole range of mole fractions at this temperature. Excess enthalpies of mixtures for halogenized aromatic + MMTSO and + DMSO were fitted with Eq. (1) by the method of least squares, and are described as solid lines in Figs. 1 and 2.

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

Table 1

Excess enthalpies H^E of halogenized aromatic + MMTSO and halogenized aromatic + DMSO at 298.15 K

x^a	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}
$(1-x)$Chlorobenzene + xMMTSO					
0.01711	45.25	0.23999	386.31	0.69661	331.57
0.05793	142.49	0.25912	396.70	0.78021	273.65
0.07334	172.94	0.41228	435.04	0.88699	163.66
0.10257	229.56	0.51377	418.56	0.90980	136.32
0.11518	249.10	0.58054	392.30	0.95623	70.086
0.14666	295.25	0.68042	344.27	0.98092	32.673
$(1-x)$Fluorobenzene + xMMTSO					
0.04351	97.25	0.39489	406.89	0.78139	229.69
0.05093	116.26	0.41200	406.66	0.80255	213.15
0.07608	162.33	0.44580	404.31	0.86396	156.65
0.08680	176.94	0.47985	401.67	0.90277	110.32
0.12374	235.30	0.54593	379.81	0.93027	81.01
0.16112	279.55	0.58855	366.22	0.96606	41.15
0.31519	387.48	0.62417	347.72		
0.24854	356.32	0.69574	298.80		
$(1-x)$Bromobenzne + xMMTSO					
0.02208	58.01	0.41827	429.34	0.72160	279.15
0.04279	106.15	0.45191	420.12	0.82246	189.95
0.09691	210.29	0.45629	424.84	0.85183	155.60
0.13387	266.39	0.51828	407.05	0.89886	110.75
0.15115	288.46	0.54015	396.18	0.93033	76.74
0.18016	326.34	0.56715	382.73	0.97901	22.90
0.22692	364.08	0.64821	330.13	0.98085	19.95
0.27363	393.29	0.67803	314.09		
0.35264	422.04	0.69637	296.87		
$(1-x)$4-Chlorotoluene + xMMTSO					
0.02576	88.19	0.39935	773.37	0.79468	416.73
0.04072	135.73	0.42860	781.85	0.84377	323.19
0.10169	315.91	0.45103	786.17	0.88106	245.17
0.11043	344.70	0.31905	727.66	0.71942	540.94
0.11984	366.50	0.39200	772.69	0.79059	424.97
0.16016	469.47	0.50199	770.88	0.92642	155.05
0.18070	517.04	0.55146	742.96	0.92855	150.03
0.19324	542.83	0.59543	703.32	0.95315	100.50
0.24977	637.27	0.64821	642.29	0.97564	49.12
0.27943	680.83	0.67945	601.65	0.98029	40.00
$(1-x)$4-Fluorotoluene + xMMTSO					
0.06268	233.32	0.40759	633.87	0.83201	330.14
0.10496	349.43	0.53911	638.03	0.86328	265.38
0.20130	509.85	0.57904	627.82	0.90599	179.74
0.22570	540.60	0.64549	580.20	0.91163	169.34
0.31767	596.40	0.73503	490.53	0.97389	46.61

Table 1 (*continued*)

x^a	H^E J mol^{-1}	x	H^E J mol^{-1}	x	H^E J mol^{-1}
(1 − x)Chlorobenzene + xDMSO					
0.03500	87.02	0.37946	497.12	0.79625	320.18
0.04769	118.85	0.47635	516.54	0.84779	253.46
0.11740	252.53	0.52769	515.18	0.88467	198.46
0.14478	295.25	0.54967	510.01	0.92467	131.15
0.16451	321.64	0.60718	488.54	0.94690	92.59
0.22573	392.48	0.65880	454.08	0.96575	59.86
0.32446	469.12	0.72477	402.17	0.98582	24.47
(1 − x)Fluorobenzene + xDMSO					
0.03930	58.55	0.21024	208.12	0.72346	205.33
0.04444	65.46	0.29404	238.04	0.80677	163.68
0.10263	130.16	0.33054	250.43	0.87078	121.32
0.10949	135.27	0.43290	259.95	0.94004	63.46
0.14786	168.16	0.56575	253.48	0.97846	23.05
0.15200	172.42	0.64049	232.45		
(1 − x)Bromobenzene + xDMSO					
0.03455	85.17	0.38436	450.22	0.89591	153.94
0.04904	117.36	0.46418	461.00	0.90544	140.42
0.13040	260.27	0.59483	435.84	0.91290	132.37
0.16670	308.14	0.60593	432.39	0.92271	116.58
0.17806	321.74	0.61948	423.02	0.97220	43.19
0.23247	378.38	0.70671	369.26	0.97897	31.26
0.27038	405.28	0.79881	280.02		
0.37822	448.98	0.83500	232.71		
(1 − x)4-Chlorotoluene + xDMSO					
0.034988	121.12	0.24739	687.63	0.81960	400.11
0.046381	158.10	0.28276	736.19	0.85812	330.35
0.07139	241.15	0.29925	758.13	0.90889	228.19
0.11141	365.11	0.41803	828.08	0.94888	136.90
0.14158	450.18	0.52183	790.12	0.98729	36.46
0.14405	457.34	0.63513	676.52		
0.17600	540.89	0.72428	557.23		
(1 − x)4-Fluorotoluene + xDMSO					
0.02490	97.86	0.28875	528.29	0.80795	356.61
0.04766	174.33	0.39205	556.92	0.85016	298.12
0.07854	261.91	0.42825	562.74	0.89569	224.57
0.12286	351.95	0.52516	556.22	0.93905	136.00
0.13746	376.41	0.60149	530.73	0.95434	103.61
0.18460	441.38	0.61142	528.57	0.98681	33.10
0.24750	502.21	0.72735	447.91		

[a] Mole fraction of the sulfide.

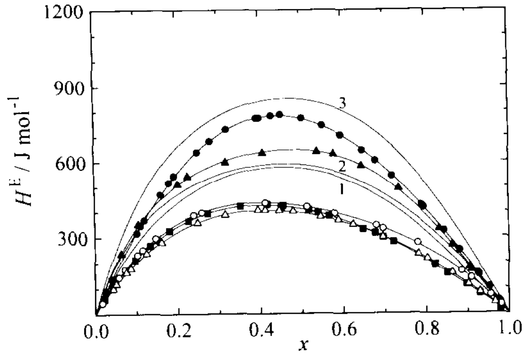

Fig. 1. Excess enthalpies of mixing at 298.15 K. △, (1 − x)chlorobenzene + xMMTSO; ○, (1 − x)fluorobenzene + xMMTSO; ■, (1 − x)bromobenzene + xMMTSO; ●, (1 − x)chlorotoluene + xMMTSO; ▲, (1 − x) fluorotoluene + xMMTSO; 1, (1 − x)benzene + xMMTSO; 2, (1 − x)toluene + xMMTSO ; 3, (1 − x)p-xylene + xMMTSO.

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

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

are given in Table 2. The excess enthalpies of benzene, toluene, p-xylene + MMTSO and + DMSO [2,6,13] are also plotted in Figs. 1 and 2 for comparison. Here, the excess enthalpies of toluene + DMSO were measured at 303.15 K [13].

Comparing the excess enthalpies of halogenized benzene + MMTSO with those of benzene + MMTSO as a reference system, the mixture of benzene + MMTSO showed the largest enthalpic unstabilization on mixing. The mixture of fluorobenzene + MMTSO

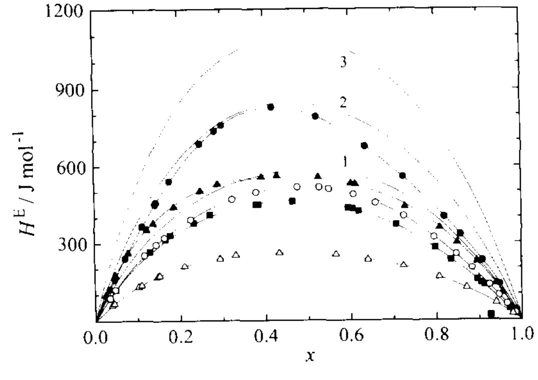

Fig. 2. Excess enthalpies of mixing at 298.15 K: △, (1 − x)chlorobenzene + xDMSO; ○, (1 − x)fluorobenzene + xDMSO; ■, (1 − x)bromobenzene + xMMTSO; ●, (1 − x)chlorotoluene + xDMSO; ▲, (1 − x)fluorotoluene + xDMSO; 1, (1 − x)benzene + xDMSO; 2, (1 − x)toluene + xDMSO; 3, (1 − x)p-xylene + xDMSO.

Table 2

Best fit values for the coefficients A_i of Eq. (1) and the calculated standard deviations of the fit s_f

System	A_1	A_2	A_3	A_4	A_5	s_f/J mol^{-1}
Chlorobenzene + MMTSO	1691.5	517.86	576.28			1.5
Fluorobenzene + MMTSO	1579.1	487.01	273.71	160.09		2.1
Bromobenzene + MMTSO	1635.6	612.20	265.40	224.89		2.5
4-Chlorotoluene + MMTSO	3079.5	796.30	−158.76	−87.72	169.36	2.6
4-Fluorotoluene + MMTSO	2585.9	175.85	547.31	1268.5		3.5
Chlorobenzene + DMSO	2070.9	118.20	169.70	365.70		1.7
Fluorobenzene + DMSO	1032.9	127.72	345.25	129.85		1.5
Bromobenzene + DMSO	1846.7	230.76	258.60	343.41		2.1
4-Chlorotoluene + DMSO	3218.4	1145.4	−9.83	−879.2		1.3
4-Fluorotoluene + DMSO	2211.5	253.47	1113.3	628.34		3.7

showed the smallest enthalpic unstabilization among the halogenized aromatic + MMTSO as shown in Fig. 1.

The effect of replacing a hydrogen in the 4-position of toluene with a halogen on excess enthalpies of toluene + MMTSO has the same sequence as the mixtures of benzene + MMTSO. The excess enthalpy of fluorobenzene or fluorotoluene + MMTSO is the smallest among the mixtures of each halogenized compound + MMTSO. These halogenized aromatic compounds have large permanent dipole moments and induced-dipole moments. The enthalpic stabilization from electrostatic interaction between those aromatics and the dipole of MMTSO might reduce the unstabilization on mixing. However, large enthalpic stabilization of dipole–dipole interaction in each pure component was also removed on mixing.

Enthalpies of mixing of toluene and halogenized toluene + MMTSO were larger than those of benzene and halogenized benzene + MMTSO for each aromatic compound. Those of halogenized toluene + MMTSO were larger than that of toluene + MMTSO. The systems of halogenized toluene + MMTSO showed that the effect of substitution with halogen on excess enthalpy was in the opposite direction compared with that of halogenized benzene + MMTSO. However, excess enthalpies of halogenized toluene + MMTSO which are equivalent to *p*-xylene replacing a methyl radical with a halogen radical were smaller than that of *p*-xylene + MMTSO. On the other hand, the volume contraction of the system of toluene + MMTSO is two to five times larger than that of halogenized toluenes + MMTSO, even that of halogenized benzenes does not show such a large difference [14]. Thus the stabilization effect of volume contraction on excess enthalpies of mixing for the system of toluene + MMTSO might be larger than the systems of halogenized toluenes + MMTSO. The volume contraction of *p*-xylene + MMTSO was, however, almost similar to halogenized toluene + MMTSO [14]. The large difference of volume contraction described above might bring the opposite effect of substituent halogen on excess enthalpies between the mixtures of halogenized benzene + MMTSO and those of halogenized toluene + MMTSO.

Excess enthalpies of halogenized aromatic compound + DMSO showed an almost similar effect on the substitution with halogen as those of aromatic halogen + MMTSO

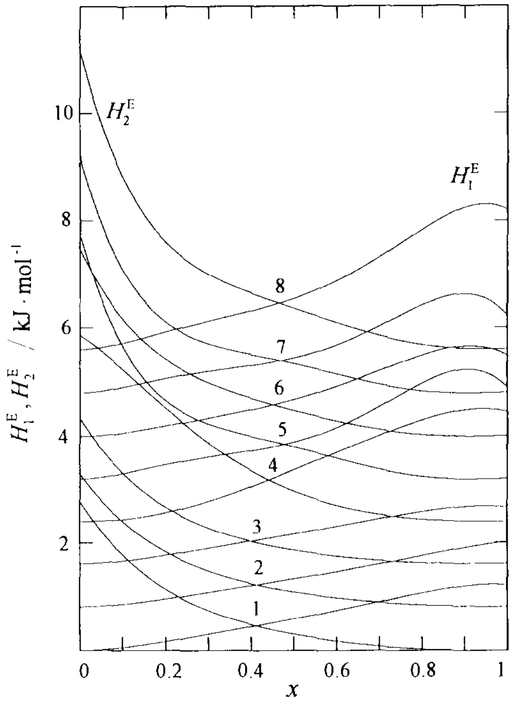

Fig. 3. Excess partial molar enthalpies at 298.15 K: 1, $(1-x)$chlorobenzene + xMMTSO; 2, $(1-x)$fluorobenzene + xMMTSO; 3, $(1-x)$bromobenzene + xMMTSO; 4, $(1-x)$chlorotoluene + xMMTSO; 5, $(1-x)$fluorotoluene + xMMTSO; 6, $(1-x)$benzene + xMMTSO; 7, $(1-x)$toluene + xMMTSO; 8, $(1-x)p$-xylene + xMMTSO. The origin of ordinate is shifted successively by 0.8 kJ mol^{-1} for each system for the sake of clarity.

(Fig. 2). Those of the mixture of toluene + DMSO, however, showed a different tendency even considering the heat capacity difference between 298.15 K and 303.15 K.

Excess partial molar enthalpies were determined from Eq. (1) and the coefficients listed in Table 2, and are plotted in Fig. 3. The mixtures of benzene, toluene and p-xylene + MMTSO reported previously [6] are also plotted for comparison. The excess partial molar enthalpies of all mixtures determined here containing MMTSO each have a maximum (halogenized aromatic compounds) and a corresponding minimum (MMTSO) in the range from $x = 0.90$ to 0.95 as shown in Fig. 3. The subscripts 1 and 2 represent the benzene derivative and MMTSO, respectively. The mixtures of benzene, toluene and p-xylene + MMTSO have similar maxima and minima at $x = 0.9$ [2,6]. The maximum and minimum of excess partial molar enthalpies were observed for all mixtures of aromatic compounds + MMTSO. It may be caused by the existence of a flexible $-CH_3-S-CH_3$ group in an MMTSO molecule. This is because there is no such anomaly in the mixtures, not only in all mixtures determined here containing DMSO but also DMSO + benzene [2], + toluene [13] and + p-xylene [15].

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies at infinite dilution were determined from Eq. (1) with the coefficients in Table 2,

Table 3

Excess partial molar enthalpies at infinite dilution at 298.15 K

System	$H_1^{E,\infty}$/kJ mol^{-1}	$H_2^{E,\infty}$/kJ mol^{-1}
Chlorobenzene(1) + MMTSO(2)	1.75	2.79
Fluorobenzene(1) + MMTSO(2)	1.21	2.50
Bromobenzene(1) + MMTSO(2)	1.06	2.74
4-Chlorotoluene(1) + MMTSO(2)	2.07	3.50
4-Fluorotoluene(1) + MMTSO(2)	1.69	4.58
Chlorobenzene(1) + DMSO(2)	1.76	2.72
Fluorobenzene(1) + DMSO(2)	1.12	1.64
Bromobenzene(1) + DMSO(2)	1.53	2.68
4-Chlorotoluene(1) + DMSO(2)	2.94	3.47
4-Fluorotoluene(1) + DMSO(2)	2.44	4.20

and summarized in Table 3. There were complicated relations between halogen radicals and the excess partial molar enthalpies at infinite dilution. The limiting excess partial molar enthalpies of the halogenized aromatic, $H_1^{E,\infty}$, of all the mixtures with MMTSO or DMSO studied were smaller than those of MMTSO or DMSO, $H_2^{E,\infty}$, respectively. A similar result had been obtained for mixtures of methylbenzenes and cycloethers + MMTSO [6,7], although the mixtures of MMTSO with oxolane [7], water [2], chloromethanes [3,4], and n-alkane-1-ols [5] were different.

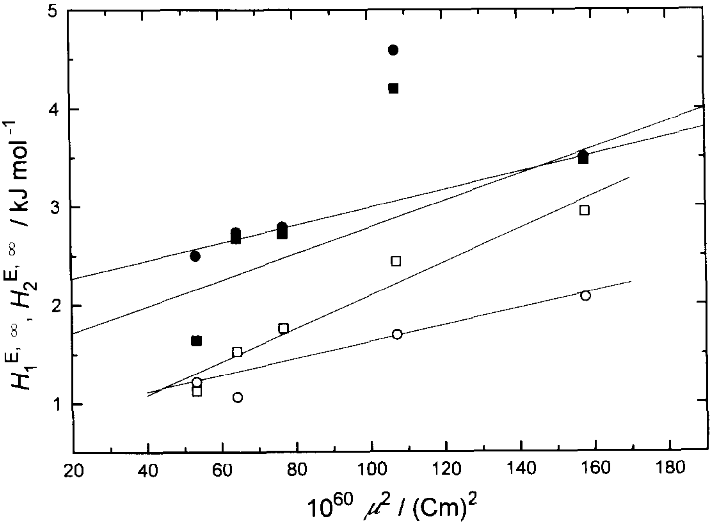

Fig. 4. Relation between limiting excess partial molar enthalpies and squares of dipole moments of the halogenized aromatic compounds. Symbols of circles and squares are the mixtures of halogenized aromatic (1) + MMTSO (2) and those of halogenized aromatic (1) + DMSO (2), respectively. Open and solid marks show $H_1^{E,\infty}$ and $H_2^{E,\infty}$, respectively.

The values of $H_1^{E,\infty}$ and $H_2^{E,\infty}$ are plotted in Fig. 4 against squares of dipole moments of halogenized aromatic [16] for the sake of understanding the effect of dipole–dipole interaction. Linear relationships were obtained as shown in Fig. 4 between the limiting excess partial molar enthalpies of the mixtures of fluorobenzene, chlorobenzene, fluorotoluene and chlorotoluene + MMTSO and + DMSO at infinite dilution and squares of dipole moments. The coefficients of Eq. (3) and the standard deviation are listed in Table 4.

$$H^{E,\infty}/\mathrm{kJ\ mol^{-1}} = a + b(\mu/\mathrm{Cm})^2 \tag{3}$$

Excess partial molar enthalpies at infinite dilution of the mixtures containing MMTSO or DMSO were increased with increasing the dipole moment of aromatic halide. The dipole–dipole interaction energy u_{12} is expressed as [17]

$$u_{12} = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{r^6kT} \tag{4}$$

Then the interaction energy due to dipole–dipole interaction is proportional to the square of dipole moment of each component. The values of enthalpic stabilization of halogenized aromatic + MMTSO or + DMSO and dipole–dipole interaction energies have good linearity for the observed mixtures of halogenized aromatic + MMTSO or + DMSO. Furthermore, the effect of dipole moment on excess partial molar enthalpies at infinite dilution of the mixtures containing MMTSO were smaller than those containing DMSO. Because DMSO molecules (dipole moment 13.4×10^{-30} Cm) [18] have larger dipolar stabilization than MMTSO molecules (10.7×10^{-30} Cm) [10] in pure liquid state, the DMSO mixtures may absorb larger heat than the MMTSO mixtures, owing to the insertion of weak polar molecules of the aromatic halides.

We reported previously [2–8], that comparing with the states before mixing, the mixtures containing MMTSO are energetically less stable or more unstable than those containing DMSO, when the other component is polar, irrespective of aprotic or protic, namely water [2], dichloromethane [3], chloroform, deuterochloroform [4], *n*-alkane-1-ols [5], and methyl alkylketones [11], and the mixtures containing DMSO are more unstable than those with MMTSO, when the second component is non-polar, $C_6H_{6-n}(CH_3)_n$, $n = 0$ to 3 [2,6] and cycloethers [7]. It was explained that the major effect

Table 4

Best fit values for the coefficients of Eq. (3)

System	$H^{E,\infty}$	a	$10^{62}b$	s_f/J mol^{-1}
Halogenized aromatic + MMTSO	$H_1^{E,\infty}$	0.772	0.852	0.24
	$H_2^{E,\infty}$	2.09	0.901	0.07[a]
Halogenized aromatic + DMSO	$H_1^{E,\infty}$	0.401	1.69	0.18
	$H_2^{E,\infty}$	1.44	1.34	0.49[a]

[a] Smoothed except the mixture of fluorotoluene. The unit of dipole moment is Cm.

on the excess enthalpies of solvent + MMTSO or + DMSO might arise from hindering of stable dipolar contacts by the non-polar radicals. However, the mixtures of halogenized aromatic + MMTSO or + DMSO have not only same effect as non-polar solvent reported previously [6] but also an additional, relatively large energetic effect from volume contraction on mixing [14].

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