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THERMODYNAMICS OF LIQUID MIXTURES CONTAINING METHYL METHYLTHIOMETHYL SULFOXIDE. VII. EXCESS ENTHALPIES OF BINARY MIXTURES BETWEEN METHYL METHYLTHIOMETHYL SULFOXIDE AND EACH OF TOLUENE, *o*-, *m*-, *p*-XYLENES AND 1,3,5-TRIMETHYLBENZENE AT 298.15 K

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SUMMARY

Excess enthalpies of five mixtures between methyl methylthiomethyl sulfoxide (MMTSO) and five methylbenzenes, *i.e.*, toluene, *o*-xylene, *m*-xylene, *p*-xylene or 1,3,5-trimethylbenzene, have been determined at 298.15 K. All the mixtures show the positive enthalpy changes over the whole range of mole fractions. Excess enthalpies of MMTSO + methylbenzenes are smaller than that of corresponding dimethyl sulfoxide(DMSO) + methylbenzenes and are increased with the increase of the number of methyl groups in the methylbenzenes. Linear relationships are obtained between the number of methyl groups of methylbenzenes and the excess partial molar enthalpies of MMTSO and benzene, toluene, *m*-xylene and 1,3,5-trimethylbenzene at infinite dilution.

INTRODUCTION

To clarify quantitatively the correlation between thermodynamic properties of mixtures and the molecular structures of their components, the excess thermodynamic functions for binary mixtures between MMTSO and water, methanol, ethanol, 1-propanol, benzene, DMSO, carbon tetrachloride, chloroform, dichloromethane, or deuterochloroform were reported(refs.1-5), as well as those of DMSO and each of water, benzene, and deuterochloroform.

In this paper, the excess enthalpies of mixtures between MMTSO and mono-, di- or tri-methylbenzene are determined over the whole range of mole fractions.

EXPERIMENTAL

Materials

The procedures of purification and the final purities of MMTSO were the same as those described previously (refs. 1, 2). Toluene (Merck, uvasol), *o*-, *m*-

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and *p*-xylene and 1, 3, 5-trimethylbenzene(Kishida, GR) were fractionally distilled over P_2O_5 or freshly activated molecular sieves 4A which had been evacuated at 423 K for 12h under 10^{-2} to 10^{-3} Pa. G.l.c. results obtained by using each 2 m column of 10 per cent SE-30 on chromosorb, 20 per cent PEG-1000 on celite 545, and Porapak Q with FID on Yanagimoto G180FP showed merely some trace-impurity peaks($<10^{-7}$). Coulometric Karl-Fischer's method on a Moisture Meter(Mitsubishi Chemical Ind., CA-02) gave the water contents of each alcohol to be 0.01 mole per cent or less.

Apparatus and procedures

A twin-microcalorimeter of heat-conduction type(laboratory designation MC-AII) (refs. 2, 6, 7) was used for measurements of excess enthalpies at 298.15 K.

Pure liquids and the mixtures were loaded from weighed gas-tight syringes (Hamilton 1001TLL or 1002TLL) fitted with suitably bent stainless-steel needles(Hamilton HF730). All mixtures were prepared by mass with a semi-microbalance in a thermostatted room. When the mixing ratio of the two liquids was larger than 1.5 cm^3/0.2 cm^3, excess enthalpies were measured by successive dilution.

After thermal equilibrium was attained, mixing was started by slow rocking of the mixing vessels in mercury pools manually and completed by the tenth rocking. This procedure of slow locking was repeated at least three times until the heat change on stirring became constant within 0.1 per cent of it. The details of calorimetric procedures and reproducibility test of this calorimeter system were described elsewhere (refs. 6, 7).

RESULTS AND DISCUSSION

Excess enthalpies

The obtained experimental results of excess enthalpies are summarized in Table 1 and Fig. 1. They were fitted with Eqn.(1) by the method of least squares.

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

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

$$s_f/(\mathrm{J\cdot mol^{-1}})=[\sum_{i=1}^{n}\{H_i^E(\mathrm{obs.})-H_i^E(\mathrm{calc.})\}^2/(n-k)]^{1/2} \qquad (2)$$

are given in Table 2.

All the excess enthalpies determined are positive over the whole range of

TABLE 1

Experimental excess enthalpies at 298.15 K

x	H_m^E (J·mol^{-1})	x	H_m^E (J·mol^{-1})	x	H_m^E (J·mol^{-1})
		(1-x)toluene + xMMTSO			
0.06935	241.48	0.43509	584.20	0.78289	367.95
0.12779	378.19	0.45758	596.52	0.81337	328.88
0.23274	499.75	0.53750	582.07	0.92625	142.85
0.27822	529.61	0.61808	541.14	0.92816	139.84
0.30694	551.66	0.72303	443.98	0.97279	54.99
0.38658	582.88	0.77932	371.07	0.97934	42.17
		(1-x)o-xylene + xMMTSO			
0.028328	118.35	0.25363	643.70	0.76674	532.12
0.052550	206.58	0.30218	700.53	0.81266	428.06
0.092263	326.02	0.41024	794.08	0.82441	399.16
0.095777	340.81	0.42407	793.70	0.93478	125.56
0.14205	450.05	0.54960	808.15	0.96702	54.47
0.20731	579.34	0.55011	810.93	0.98012	31.86
0.23023	613.31	0.67287	698.26		
		(1-x)m-xylene + xMMTSO			
0.03772	224.20	0.34155	681.56	0.74955	608.22
0.07713	425.19	0.41211	875.00	0.85753	396.97
0.08148	436.51	0.47359	856.12	0.89058	321.99
0.16653	687.09	0.50940	849.35	0.95136	129.77
0.26681	817.05	0.56150	822.48	0.97959	52.79
0.28371	830.79	0.68301	705.18		
		(1-x)p-xylene + xMMTSO			
0.02223	116.18	0.33822	812.88	0.71777	662.49
0.07205	333.79	0.38543	830.51	0.82757	444.18
0.10993	450.19	0.47125	848.39	0.92791	191.92
0.22471	694.92	0.57439	824.06	0.94446	149.39
0.26823	749.45	0.68783	709.33	0.97746	59.50
		(1-x)1,3,5-trimethylbenzene + xMMTSO			
0.07057	444.21	0.41029	1015.9	0.78525	761.13
0.15246	722.19	0.49374	1035.7	0.84449	598.85
0.24782	888.88	0.58072	1038.1	0.93542	252.79
0.29836	947.21	0.63416	1002.3	0.98053	72.82
0.31897	964.79	0.64092	998.60		
0.37069	991.76	0.71142	922.60		

mole fractions at this temperature. Enthalpic destabilization on mixing is increased with increasing the number of methyl groups in the molecules of components. Among the mixtures of xylene isomers and MMTSO, enthalpic destabilization of o-xylene + MMTSO is the smallest and that of m-xylene + MMTSO is the largest in xylene-rich region. In MMTSO-rich region, however, *m*- and *p*-xylenes behave similar.

TABLE 2

Best-fit values for the coefficients A_i of Eqn.(1) and calculated standard deviation of the fit s_f

Mixture	A_1	A_2	A_3	A_4	A_5	A_6	s_f (J·mol^{-1})
toluene + MMTSO	2350.0	334.8	352.3	867.6	581.8		4.0
o-xylene + MMTSO	3285.7	-7.9	-305.8	1563.4			4.0
m-xylene + MMTSO	3400.3	708.9	1571.8	1376.3	-357.6		3.5
p-xylene + MMTSO	3389.9	360.3	703.5	1138.5			3.3
mesitylene + MMTSO	4164.3	-198.4	1970.1	1468.5	-219.6	1094.2	4.7
benzene + MMTSO[a]	2291.3	401.1	187.5	599.6			4.3

[a] Cited for comparison from reference [2]

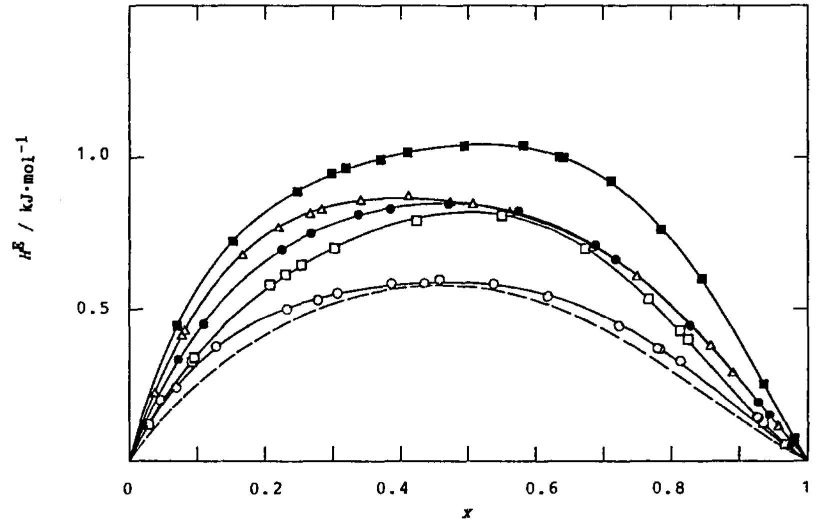

Fig. 1 Excess enthalpies at 298.15 K: ○ ,(1-x)toluene + xMMTSO; □ , (1-x)*o*-xylene + xMMTSO; △ , (1-x)*m*-xylene + xMMTSO; ● ,(1-x)*p*-xylene + xMMTSO; ■ , (1-x)1,3,5-trimethylbenzene + xMMTSO; — — — , (1-x)benzene + xMMTSO (ref. 2).

Excess partial molar enthalpies

Excess partial molar enthalpies were determined from Eqn.(1) and the coefficients listed in Table 2 and plotted in Fig. 2. The excess partial molar enthalpies of all the mixtures determined here have each couple of a maximum(benzene derivative) and a corresponding minimum (MMTSO) in the range from x_2=0.85 to 0.95 as shown in Fig. 2. The subscripts 1 and 2 represent the benzene derivative and MMTSO, respectively. The mixture of benzene + MMTSO reported already has similar maximum and minimum at x_2=0.9 (ref. 2). 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_2-S-CH_3 group in an MMTSO molecule. This is because there is no such anomaly in the mixtures of DMSO + benzene (ref. 2), + *p*-xylene and + 1,3,5-trimethylbenzene (ref. 9).

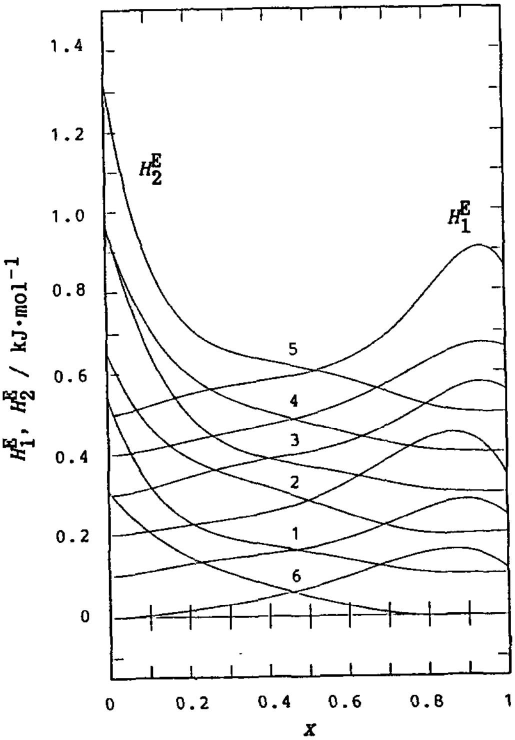

Fig. 2 Excess partial molar enthalpies at 298.15 K: 1, (1-x)toluene + xMMTSO; 2, (1-x)*o*-xylene + xMMTSO; 3, (1-x)*m*-xylene + xMMTSO; 4, (1-x)*p*-xylene + xMMTSO; 5, (1-x)1,3,5-trimethylbenzene + xMMTSO; and 6, (1-x)benzene + xMMTSO(ref. 2). The origin of ordinate is shifted successively by 100 J·mol^{-1} for each system for the sake of clarity.

Excess partial molar enthalpies at infinite dilution were also calculated from Eqn.(1) with the coefficients in Table 2, and summarized in Table 3. The excess partial molar enthalpies at infinite dilution, $H_1^{E,\infty}$ and $H_2^{E,\infty}$, are plotted against number of methyl groups of methylbenzenes in Fig. 3. Linear relationships were obtained between the excess partial molar enthalpies of MMTSO and methylbenzenes at infinite dilution and number of methyl groups of toluene,

TABLE 3

Excess partial molar enthalpies at infinite dilution obtained from Eqn.(1) with the coefficients from Table 2

Mixture	$H_1^{E,\infty}$ (kJ·mol^{-1})	$H_2^{E,\infty}$ (kJ·mol^{-1})
toluene + MMTSO	2.08	4.49
o-xylene + MMTSO	1.42	4.54
m-xylene + MMTSO	2.53	6.70
p-xylene + MMTSO	2.59	5.59
mesitylene + MMTSO	3.55	8.28
benzene + MMTSO[a]	1.48	3.48

[a] Cited from reference [2].

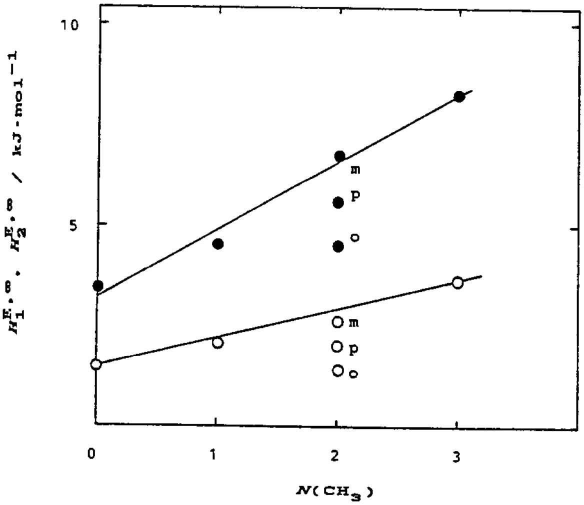

Fig. 3 Limiting excess partial molar enthalpies at infinite dilution as a function of the number of methyl group in components: $H_1^{E,\infty}$ and $H_2^{E,\infty}$ are represented by open and filled drawing, respectively.

m-xylene, 1,3,5-trimethylbenzene and benzene(ref. 2), as shown by the two straight lines in Fig. 3. These relationships can be expressed as

$$H_1^{E,\infty}\ /\ \mathrm{kJ\cdot mol^{-1}} = 1.41 + 0.67N(\mathrm{CH_3}),\quad s_f/\mathrm{kJ\cdot mol^{-1}}=0.15 \qquad (3)$$

$$H_2^{E,\infty}\ /\ \mathrm{kJ\cdot mol^{-1}} = 3.25 + 1.66N(\mathrm{CH_3})\quad s_f/\mathrm{kJ\cdot mol^{-1}}=0.28 \qquad (4)$$

Limiting excess partial molar enthalpies of MMTSO in benzene, toluene, and meta-substituted methylbenzenes were increased by 1.7 kJ·mol^{-1} per methyl group, although the benzene rings have quadrupole moment and induced-dipole moment. On the other hand, limiting excess partial molar enthalpies of the methylbenzenes in MMTSO were increased by 0.67 kJ·mol^{-1} per methyl group, as shown in Fig. 3. The limiting excess partial molar enthalpies of benzene and *o*-xylene were almost the same.

Although the excess enthalpies were positive, the present mixtures may show large volume contraction, since the excess volume of benzene + MMTSO is negative and large (ref. 1). For a comprehensive study of the systems, measurements of the excess volume are at present being undertaken in the laboratory.

Concludingly, the mixtures containing MMTSO were less unstable than those of DMSO, when the other component is non-polar, as shown in Fig. 4, where excess enthalpies of DMSO + *p*-xylene and DMSO + 1,3,5-trimethylbenzene are cited for comparison (ref. 9). The major reason for this might be the lesser decrease of stabilization of dipole-dipole interaction due to dilution by non-polar molecules. The dipole-dipole stabilization of pure MMTSO (μ=10.$_7$X10^{-30}C·m) (ref. 10) may be smaller than that of DMSO(μ=13.4X10^{-30}C·m) (ref. 11). However, the

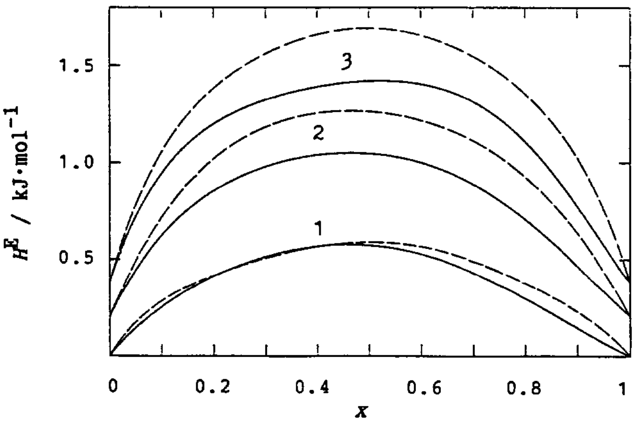

Fig. 4 Excess enthalpies of mixtures of MMTSO and those of DMSO at 298.15 K: 1, benzene; 2, *p*-xylene; 3, 1,3,5-tri-methylbenzene; ———, MMTSO; – – –, DMSO. The origin of ordinate is shifted successively by 200 J·mol^{-1} for each system for the sake of clarity.

mixtures containing MMTSO were less stable or more unstable than those of DMSO, when the other component was polar, irrespective of aprotic or protic, namely water (ref. 2), chloroform, deuterochloroform (ref. 4), dichloromethane (ref. 3), n-alkylalcohols (ref. 5), or methyl alkylketones (ref. 8).

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