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Excess enthalpies of alkane-1-amines $\{C_nH_{2n+1}NH_2, n = 3–8\}$ + methyl methylthiomethyl sulfoxide and +dimethyl sulfoxide at 298.15 K

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Abstract

Excess enthalpies of binary mixtures between each of alkane-1-amines $\{C_nH_{2n+1}NH_2, n = 3–8\}$ and methyl methylthiomethyl sulfoxide (MMTSO) or dimethyl sulfoxide (DMSO) have been determined at 298.15 K. All mixtures showed positive enthalpy changes over the whole range of mole fractions.

The limiting excess partial molar enthalpies of the aliphatic amines, $H_1^{E,\infty}$, of all the mixtures with MMTSO or DMSO studied were smaller than those of MMTSO or DMSO, $H_2^{E,\infty}$, respectively. Linear relations are obtained between limiting excess partial molar enthalpies and number of methylene groups.

Keywords: Excess enthalpy; Alkane-1-amines; $\{C_nH_{2n+1}NH_2, n = 3–8\}$; Methyl methylthiomethyl sulfoxide; Dimethyl sulfoxide

1. Introduction

In our previous papers [1–13], 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 ($C_nH_{2n+1}OH$, $n = 1–9$), six methyl-benzenes $\{C_6H_{6-n}(CH_2)_n, n = 1–3\}$, six cycloethers, three aliphatic-ethers, five monohalogenated aromatic compounds (benzene and toluene), six *o*- and *m*-dihalogenated benzenes and those of DMSO were reported.

For further information about thermodynamic properties of the mixtures and molecular structures of their components, particularly comparing the above correlations with those of the mixtures of alcohols, excess enthalpies of the mixtures between MMTSO and some aliphatic amines $\{C_nH_{2n+1}NH_2, n = 3–8\}$ were determined over the whole range of mole fractions. Those of amines + 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 (Cica-Merck, uvasol) were the same as those described previously [1,2]. Aliphatic amines ($C_nH_{2n+1}NH_2$, $n = 3–8$, Tokyo Kassei, GR) were fractionally distilled over freshly activated molecular sieves 4 Å which had been

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evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa. G.l.c. 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 calorimetric procedures and reproducibility test of this calorimeter system were described elsewhere [2,13,14].

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 of aliphatic amines + MMTSO and +DMSO observed were positive over the whole range of mole fractions at this temperature. Excess enthalpies of mixtures for aliphatic amines + 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.

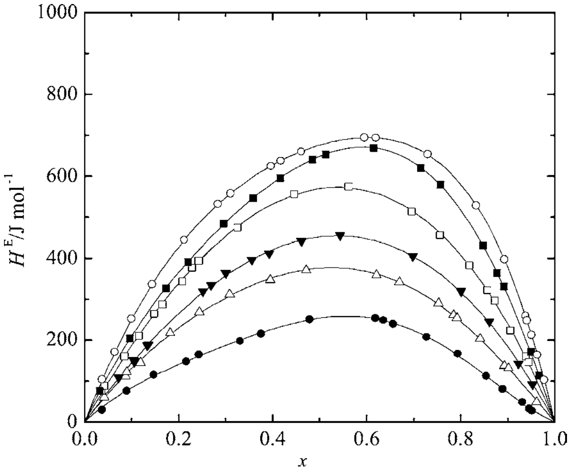

Fig. 1. Excess enthalpies of $(1 - x)C_nH_{2n-1}NH_2 + x$MMTSO ($n = 3$–8) at 298.15 K. (●) $n = 3$; (△) $n = 4$; (▼) $n = 5$; (□) $n = 6$; (■) $n = 7$; (○) $n = 8$.

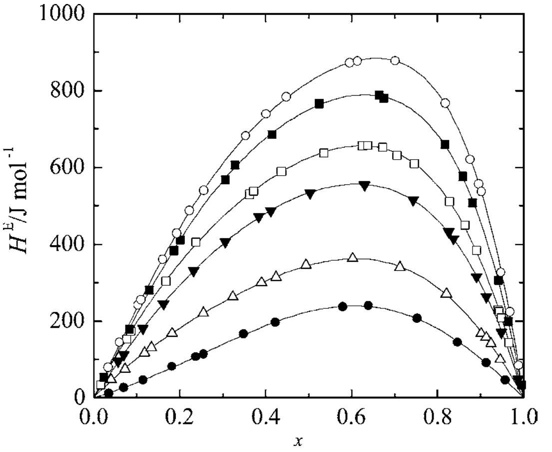

Fig. 2. Excess enthalpies of $(1 - x)C_nH_{2n-1}NH_2 + x$DMSO ($n = 3$–8) at 298.15 K. (●) $n = 3$; (△) $n = 4$; (▼) $n = 5$; (□) $n = 6$; (■) $n = 7$; (○) $n = 8$.

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

The coefficients A_i in Eq. (1) and standard deviations of the fits are given in Table 2. The excess enthalpies of amine + MMTSO increased with increasing size of aliphatic groups of aliphatic amines, just as in the mixtures of alkane-1-ol + MMSTO [5]. Excess enthalpies of aliphatic amine compounds + DMSO showed a similar effect on the substitution with aliphatic groups as those of aliphatic amines + MMTSO. The major reason for this might be not only the smaller decrease of stabilization of dipole–dipole due to dilution by aliphatic surface but also the increase of intermolecular dipole–dipole and dipole–induced dipole interaction between sulfides and amines.

Excess enthalpies of propane-1-amine + MMTSO and butane-1-amine + MMTSO were larger than those of propane-1-amine + DMSO and butane-1-amine + DMSO, respectively. However, excess enthalpies of the MMTSO containing aliphatic amines from pentane-1-amine to octane-1-amine measured were smaller than those of DMSO containing aliphatic amines from pentane-1-amine to octane-1-amine, respectively.

For the sake of an elementary consideration of pairwise interaction, excess partial molar enthalpies at

Table 1
Excess enthalpies H^E of aliphatic amines + MMTSO and +DMSO at 298.15 K

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
$(1-x)$propane-1-amine + xMMTSO					
0.03642	28.98	0.08977	76.34	0.14661	115.46
0.21658	148.45	0.24292	165.22	0.33089	197.94
0.37561	215.56	0.47824	251.25	0.61807	253.43
0.63583	248.59	0.65679	239.57	0.72756	207.76
0.79341	166.93	0.85445	112.64	0.88973	79.92
0.93186	48.56	0.94551	32.85	0.95213	27.32
$(1-x)$butane-1-amine + xMMTSO					
0.04188	60.51	0.08656	111.67	0.08920	121.34
0.11835	145.49	0.18191	216.93	0.24403	268.06
0.30851	312.23	0.39486	347.35	0.47154	371.35
0.62113	359.20	0.66958	340.97	0.75331	290.18
0.78528	261.88	0.79283	254.80	0.84111	203.45
0.89322	137.89	0.90199	131.59	0.96124	48.41
$(1-x)$pentane-1-amine + xMMTSO					
0.07260	108.83	0.10385	150.77	0.10607	147.54
0.13262	187.77	0.13524	188.59	0.25172	318.55
0.26931	334.02	0.30051	363.95	0.35555	396.85
0.39257	412.16	0.46139	442.11	0.54410	455.45
0.69822	405.18	0.80125	319.37	0.86068	245.07
0.92328	142.20	0.95296	91.16		
$(1-x)$hexane-1-amine + xMMTSO					
0.03622	75.95	0.04250	88.66	0.08389	161.03
0.11604	210.58	0.14782	264.20	0.16519	287.02
0.20695	343.61	0.22803	376.87	0.24242	394.98
0.32520	474.79	0.44568	556.41	0.56114	574.91
0.69592	514.29	0.75573	456.27	0.81818	383.02
0.85662	323.12	0.87214	297.32	0.90577	224.68
0.93792	160.13	0.94494	146.12		
$(1-x)$heptane-1-amine + xMMTSO					
0.03186	75.32	0.09616	204.10	0.17250	327.50
0.21940	392.02	0.29655	484.13	0.35864	547.08
0.41610	596.06	0.48424	640.47	0.51273	653.78
0.61465	669.17	0.71611	620.39	0.75670	578.72
0.84786	431.36	0.87784	365.33	0.89208	330.76
0.94900	171.56	0.96688	114.55		
$(1-x)$octane-1-amine + xMMTSO					
0.03716	104.26	0.06369	170.98	0.09946	251.58
0.14321	336.87	0.21138	444.58	0.28382	531.53
0.31035	557.55	0.39677	624.80	0.41759	637.48
0.46083	659.88	0.59539	694.53	0.61966	694.09
0.73029	653.50	0.83358	528.77	0.89329	397.26
0.93819	259.28	0.94139	247.95	0.95099	212.71
0.96341	164.14	0.97808	102.22		
$(1-x)$propane-1-amine + xDMSO					
0.03528	10.90	0.07009	26.54	0.11472	46.09
0.18193	80.86	0.23733	106.48	0.25519	113.06
0.34872	165.79	0.42245	196.24	0.57938	236.71
0.63902	239.26	0.75248	207.06	0.84650	144.46
0.91301	90.21	0.95741	46.39		

Table 1 (*Continued*)

x	H^{E} ($\mathrm{J\,mol^{-1}}$)	x	H^{E} ($\mathrm{J\,mol^{-1}}$)	x	H^{E} ($\mathrm{J\,mol^{-1}}$)
$(1-x)$butane-1-amine $+\,x$DMSO					
0.03998	46.88	0.07291	74.88	0.11794	117.20
0.13367	130.87	0.18150	167.34	0.25537	221.18
0.32340	262.62	0.38995	299.53	0.42408	313.81
0.49371	345.31	0.60231	362.67	0.71286	339.23
0.82058	270.21	0.90149	167.34	0.91278	156.70
0.92407	140.86	0.94579	99.12		
$(1-x)$pentane-1-amine $+\,x$DMSO					
0.05658	95.24	0.07056	112.32	0.11386	180.33
0.16151	244.82	0.23199	331.05	0.30576	406.62
0.38416	471.73	0.41200	486.38	0.50294	532.61
0.62956	553.77	0.74324	514.70	0.82556	432.01
0.83693	414.76	0.89063	315.79	0.91376	263.38
0.94825	170.38	0.98733	48.53		
$(1-x)$hexane-1-amine $+\,x$DMSO					
0.01599	33.20	0.07596	152.20	0.08609	173.78
0.16782	303.61	0.23810	404.96	0.36171	529.30
0.37159	537.11	0.43670	588.69	0.53481	637.70
0.62496	656.12	0.63641	657.23	0.67215	652.34
0.70508	630.37	0.74543	609.36	0.82702	510.59
0.86387	449.46	0.89008	384.28	0.93979	229.73
0.94215	224.84	0.94781	208.61	0.96605	143.89
$(1-x)$heptane-1-amine $+\,x$DMSO					
0.02328	53.35	0.08278	178.36	0.12823	280.62
0.18648	383.39	0.20050	411.25	0.30599	567.91
0.32838	605.34	0.41390	685.77	0.52439	766.15
0.66445	787.17	0.67507	780.35	0.81619	659.75
0.85772	576.14	0.88138	508.11	0.94124	306.19
0.96430	198.99	0.99458	33.92		
$(1-x)$octane-1-amine $+\,x$DMSO					
0.03285	79.43	0.05994	144.33	0.10254	241.04
0.11054	254.72	0.16040	360.26	0.19335	427.68
0.22276	487.26	0.25635	539.41	0.35352	681.22
0.40145	739.01	0.44786	783.05	0.59506	871.90
0.61327	876.25	0.70094	876.87	0.81823	766.63
0.87612	619.97	0.89567	556.35	0.90188	536.16
0.94774	326.44	0.96849	222.80	0.98768	84.04

infinite dilutions were determined from Eq. (1) with the coefficients in Table 2, and summarized in Table 3. The limiting excess partial molar enthalpies of aliphatic amines + MMTSO and +DMSO increased with increasing size of the aliphatic groups. The limiting excess partial molar enthalpies of the aliphatic amines $H_1^{\mathrm{E},\infty}$, of all mixtures with MMTSO or DMSO except $C_3H_7NH_2$ or $C_4H_9NH_2$ + MMTSO were larger than those of MMTSO or DMSO $H_2^{\mathrm{E},\infty}$, respectively.

The similar result was obtained for the mixtures of methylbenzenes and cycloethers + MMTSO [6,7], although the mixtures of MMTSO with oxolane [7], water [2], chloromethanes [3,4], and alkane-1-ols [5] were different. The limiting excess partial molar enthalpies of the amines at infinite dilution $H_1^{\mathrm{E},\infty}$ for aliphatic amines + MMTSO were less unstable than those for the aliphatic amines + DMSO for all mixture of aliphatic amines measured.

The hydrophobicity of aliphatic amine may depend on the number of CH_2 functional groups in the aliphatic amines. Correlation between partial molar enthalpies at infinite dilution and the number of CH_2

Table 2
Best-fit values for the coefficients A_i of Eq. (1) with the calculated standard deviations of the fit, s_f

System	A_1	A_2	A_3	A_4	s_f (J mol^{-1})
$(1-x)C_3H_7NH_2 + x$MMTSO	1014.5	−316.9	−224.7	621.3	3.1
$(1-x)C_4H_9NH_2 + x$MMTSO	1503.8	−165.4	−51.0	231.5	3.6
$(1-x)C_5H_{11}NH_2 + x$MMTSO	1808.7	−274.6	35.5	−2.0	3.3
$(1-x)C_6H_{13}NH_2 + x$MMTSO	2278.0	−340.3	152.6	−53.7	3.5
$(1-x)C_7H_{15}NH_2 + x$MMTSO	2594.7	−930.3	461.7	381.1	3.9
$(1-x)C_8H_{17}NH_2 + x$MMTSO	2705.3	−685.2	1237.2	−316.8	3.1
$(1-x)C_3H_7NH_2 + x$DMSO	896.7	−543.3	−174.1	174.1	2.0
$(1-x)C_4H_9NH_2 + x$DMSO	1379.9	−609.3	232.5	173.3	2.3
$(1-x)C_5H_{11}NH_2 + x$DMSO	2132.6	−775.5	632.6	−275.8	2.1
$(1-x)C_6H_{13}NH_2 + x$DMSO	2498.3	−965.1	897.0	−213.5	3.6
$(1-x)C_7H_{15}NH_2 + x$DMSO	3001.2	−1117.7	1164.9	−852.0	3.6
$(1-x)C_8H_{17}NH_2 + x$DMSO	3288.5	−1409.8	1590.4	−1156.2	3.8

groups were plotted in Fig. 3. Partial molar enthalpies at infinite dilution and the number of CH_2 groups are were fitted with Eq. (2) by the method of least squares, and are described as solid lines in Fig. 3 and listen in Table 4.

$$H_1^{E,\infty}, H_2^{E,\infty} = (a + b)Nc \qquad (2)$$

Coefficient b in Eq. (2) might show the size effect of aliphatic groups on partial molar enthalpies. All coefficients b determined were positive and showed unfavorable interaction between sulfides and aliphatic groups of CH_2. The size of CH_2 group might induce the enhancement of unfavorable interaction between sulfides and aliphatic amines. Coefficients b of partial molar enthalpies of the mixtures of DMSO were larger than those of the mixtures of MMTSO. On the other hand, coefficients a in Eq. (2) might show the effect of amine groups on partial molar enthalpies. All coefficients a determined were negative and showed favorable interaction between sulfides and amines. Coefficients a of partial molar enthalpies of the mixtures of DMSO were smaller than those of the mixtures of MMTSO. The amphiphiles of aliphatic amines have two opposite interaction between sulfides. There might

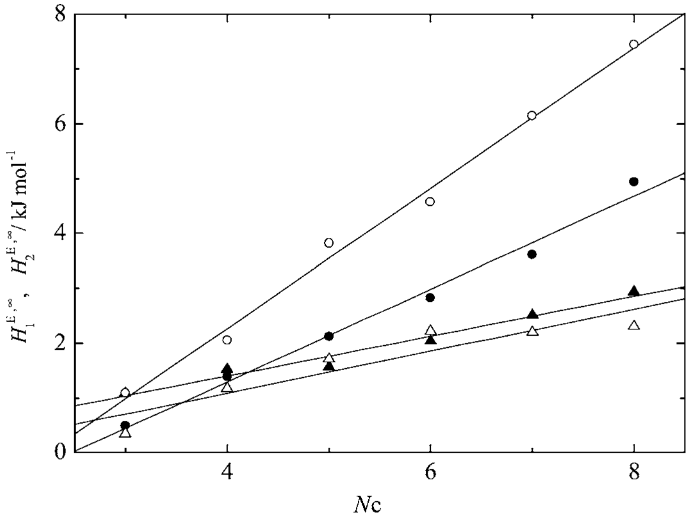

Fig. 3. Correlation between the limiting partial molar excess enthalpies and number of methylene groups of aliphatic amines. (●) $H_1^{E,\infty}$ (MMTSO) (kJ mol^{-1}); (▲) $H_2^{E,\infty}$ (MMTSO) (kJ mol^{-1}); (○) $H_1^{E,\infty}$ (DMSO) (kJ mol^{-1}); (△) $H_2^{E,\infty}$ (DMSO) (kJ mol^{-1}).

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})
$(1-x)C_3H_7NH_2 + x$MMTSO	0.49	1.09
$(1-x)C_4H_9NH_2 + x$MMTSO	1.39	1.52
$(1-x)C_5H_{11}NH_2 + x$MMTSO	2.12	1.57
$(1-x)C_6H_{13}NH_2 + x$MMTSO	2.82	2.04
$(1-x)C_7H_{15}NH_2 + x$MMTSO	3.61	2.51
$(1-x)C_8H_{17}NH_2 + x$MMTSO	4.94	2.94
$(1-x)C_3H_7NH_2 + x$DMSO	1.09	0.35
$(1-x)C_4H_9NH_2 + x$DMSO	2.05	1.18
$(1-x)C_5H_{11}NH_2 + x$DMSO	3.82	1.71
$(1-x)C_6H_{13}NH_2 + x$DMSO	4.57	2.22
$(1-x)C_7H_{15}NH_2 + x$DMSO	6.14	2.20
$(1-x)C_8H_{17}NH_2 + x$DMSO	7.44	2.31

Table 4
Best-fit values for the coefficients of Eq. (2)

	MMTSO		DMSO	
	a (kJ mol^{-1})	b (kJ mol^{-1})	a (kJ mol^{-1})	b (kJ mol^{-1})
$H_1^{E,\infty}$	−2.09	0.846	−2.85	1.27
$H_2^{E,\infty}$	−0.049	0.363	−0.439	0.382

Table 5
Physical properties of aliphatic amines and sulfoxides used

	$10^{30}\mu$ (C m)	$10V$ (nm^3)	r (nm)
Propane-1-amine	4.85	3.09	0.419
Butane-1-amine	4.83	3.62	0.443
Pentane-1-amine	4.82	4.16	0.463
Hexane-1-amine	4.80	4.70	0.482
Heptane-1-amine	4.79	5.25	0.500
Octane-1-amine	4.79	5.78	0.517
MMTSO	8.2	4.00	0.737
DMSO	13.2	2.92	0.412
MMTSO [15]	10.7		
DMSO [17]	13.4		

not be small dipole–dipole interaction effects on the limiting excess partial molar enthalpies of the mixtures between amines and sulfides. The dipole–dipole interaction energy of pair molecules [16] were shown as:

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

where μ, r and k are dipole moment, distance between molecules and Boltzman coefficient, respectively. The molecular shape of sulfides and aliphatic amines are not spheric, but as a first approximation, all molecules were treated as spheric molecules. The values of r for each system calculated as sum of radius of sphere for pair molecules are listed in Table 4.

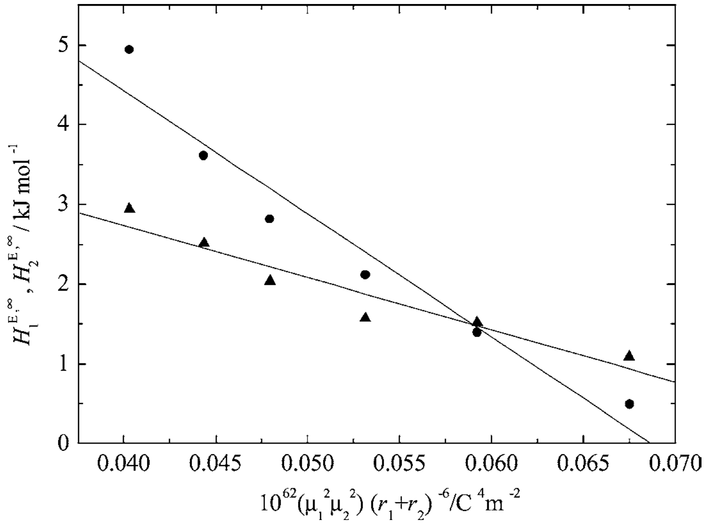

Fig. 4. Correlation between partial molar excess enthalpies at infinite dilution and $\mu_1^2\mu_2^2/(r_1+r_2)^6$ of aliphatic amines + MMTSO. (●) $H_1^{E,\infty}$ (MMTSO); (▲) $H_2^{E,\infty}$ (MMTSO).

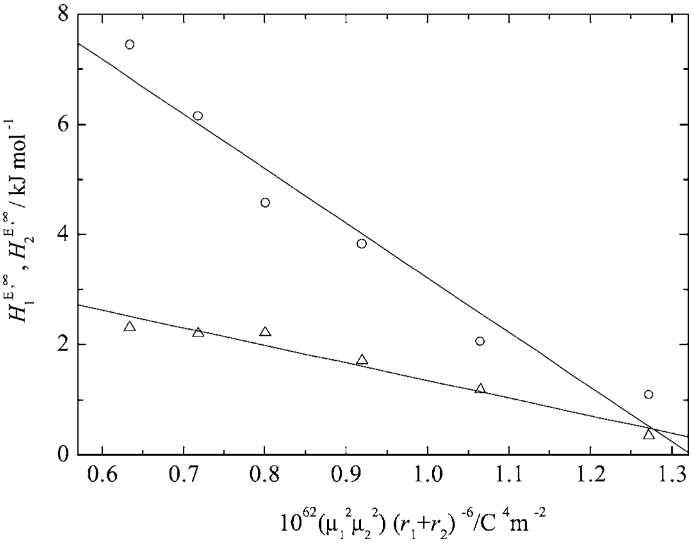

Fig. 5. Correlation between partial molar excess enthalpies at infinite dilution and $\mu_1^2\mu_2^2/(r_1+r_2)^6$ of aliphatic amines + DMSO: (○), $H_1^{E,\infty}$ (DMSO); (△), $H_2^{E,\infty}$ (DMSO).

All dipole moments of aliphatic amines have not been reported. The dipole of aliphatic amines were calculated by HyperChem [19] after geometry optimization of molecular shapes of these aliphatic amines, and are listed in Table 5. The geometry optimization were carried out by calculations using the AM1 method. The calculated value and observed one of dipole moment of MMTSO and DMSO showed closed agreement.

Linear relationships were obtained as shown in Figs. 4 and 5 between the limiting excess partial molar enthalpies of the mixtures of aliphatic amines and dipolar interaction energy terms of $\mu_1^2\mu_2^2/(r_1+r_2)^6$. The coefficients of Eq. (4) and the standard deviations are listed in Table 6.

$$H^{E,\infty}\,(\mathrm{kJ\,mol^{-1}}) = a + b\frac{\mu_1^2\mu_2^2}{(r_1+r_2)^6} \qquad (4)$$

Excess partial molar enthalpies at infinite dilution of the mixtures containing MMTSO or DMSO decreased with increasing the dipolar interaction energy terms between sulfides and amines. As shown in Table 6, coefficients b of amines + DMSO in Eq. (4) were larger than those of amines + MMTSO. DMSO molecule has not only the smallest volume and the largest dipole moment but also the most spherical molecule. Therefore, the terms of $\mu_1^2\mu_2^2/(r_1+r_2)^6$ of mixtures including DMSO might become larger than those including MMTSO. Then the coefficient b in Eq. (4) for the mixtures including DMSO were smaller than those of MMTSO.

DMSO molecules (dipole moment: 13.4×10^{-30} C m) have larger dipolar stabilization than MMTSO molecules (10.7×10^{-30} C m) in pure liquid state, the DMSO mixtures may absorb larger heat

Table 6
Best-fit values for the coefficients of Eq. (4)

System	$H_1^{E,\infty}$			$H_2^{E,\infty}$		
	a (kJ mol^{-1})	b (kJ mol^{-1} C^{-4} m^2)	s_d (kJ mol^{-1})	a (kJ mol^{-1})	b (kJ mol^{-1} C^{-4} m^2)	s_d (kJ mol^{-1})
MMTSO + amine	10.6	−154	0.4	5.3	−66	0.2
DMSO + amine	13.1	−9.9	0.6	4.6	−3.2	0.2

than the MMTSO mixtures, owing to the insertion of weak polar molecules of the amines.

It was explained that the major effect on the excess enthalpies of solvent + MMTSO or +DMSO might arise from hindering of stable dipolar–dipolar contacts by the less polar components. However, the mixtures of aliphatic amines + MMTSO or +DMSO have not only the same effect as non-polar solvent from aliphatic part reported previously [6] but also additional, relatively large energetic effect from volume contraction on mixing [18].

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