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論 文

Excess Enthalpies of Some Nitrile Compounds + Methyl Methylthiomethyl Sulfoxide or + Dimethyl Sulfoxide at 298.15 K

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Excess enthalpies of binary mixtures between each of acetonitrile, propionitrile, butyronitrile, pentanenitrile and benzonitrile + methyl methylthiomethyl sulfoxide (MMTSO) and + dimethyl sulfoxide (DMSO) have been determined at 298.15 K. All mixtures showed positive enthalpy change over the whole range of mole fractions except acetonitrile + DMSO over 0.95 in mole fraction of DMSO.

Partial molar enthalpies of the mixtures of acetonitrile (1) + DMSO (2) around 0.65 in mole fraction have maximum of H_1^E and minimum of H_2^E. Linear relations are obtained between limiting excess partial molar enthalpies and $(\mu_1^2\ \mu_2^2)(r_1+r_2)^{-6}$ except the mixtures containing for benzonitrile. However limiting excess partial molar enthalpies of the mixtures of aromoatic compounds + MMTSO or + DMSO showed good relation with $(\alpha_2\mu_1^2+\alpha_1\mu_2^2)(r_1+r_2)^{-6}$.

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, alkane-1-ols ($C_nH_{2n+1}OH$, $n=1$ to 9), alkane-1-amines ($C_nH_{2n+1}NH_2$, $n=3$ to 8), six methylbenzenes {$C_6H_{6-n}(CH_3)_n$, $n=1$ to 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.

To know further informations between thermodynamic properties of the mixtures and molecular structures of their components, particularly comparing the above correlations with those of the mixtures of amines, excess enthalpies of the mixtures between MMTSO and some aliphatic nitriles (acetonitrile, propionitrile, butyronitrile and pentanenitrile) and benzonitrile were determined over the whole range of mole fractions. Those of nitriles + 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] Acetonitrile, propionitrile, butyronitrile, pentanenitrile and benzonitrile (Kishida, GR) were fractionally distilled over freshly activated molecular sieves 4A which had been 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 per cent SE-30 on chromosorb and 20 per cent 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 mole percent 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

Table 1 Excess enthalpies of nitriles + MMTSO and + DMSO 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}
$(1-x)$acetonitrile + x MMTSO					
0.01707	41.91	0.32851	403.76	0.76612	265.95
0.06304	137.49	0.40485	421.01	0.82578	207.85
0.07978	66.68	0.45572	422.74	0.87185	157.15
0.13593	251.18	0.56283	396.45	0.91932	100.80
0.18370	309.57	0.64384	360.85	0.97444	31.74
0.25314	363.88	0.69519	323.73		
$(1-x)$propionitril + x MMTSO					
0.01668	48.32	0.18235	379.15	0.81290	296.83
0.02192	62.00	0.23390	436.89	0.88707	192.17
0.03446	94.66	0.31024	500.54	0.90635	163.85
0.04512	22.60	0.43935	535.43	0.92137	139.60
0.06345	165.97	0.52829	522.89	0.96348	68.15
0.09470	232.957	0.63373	470.02	0.97990	37.55
0.11101	263.98	0.70677	412.01		
$(1-x)$butyronitirile + x MMTSO					
0.01850	57.97	0.38917	586.56	0.70531	470.09
0.03821	114.32	0.44923	596.16	0.78771	371.99
0.07328	203.89	0.50279	595.82	0.84265	293.01
0.12801	320.16	0.53802	583.16	0.87667	236.11
0.12878	321.57	0.54993	577.16	0.90792	179.99
0.15099	361.69	0.61922	541.04	0.95587	88.90
0.21097	455.89	0.65843	509.12	0.96982	64.00
0.27325	523.53	0.69847	480.09		
$(1-x)$pentanenitrile + x MMTSO					
0.02002	69.60	0.23973	551.30	0.78204	463.99
0.04475	145.89	0.31654	633.06	0.84626	352.99
0.08505	259.50	0.41168	687.12	0.86443	318.96
0.11839	339.10	0.53122	691.06	0.89621	251.90
0.14693	400.30	0.65084	624.01	0.93437	163.99
0.19930	494.30	0.71998	551.15	0.97697	61.31
$(1-x)$benzonitrile + x MMTSO					
0.02307	37.17	0.16048	190.99	0.72452	180.82
0.03361	52.68	0.22044	230.87	0.79848	141.74
0.05330	82.07	0.29961	258.79	0.83365	118.45
0.07721	111.28	0.34169	269.28	0.89485	77.34
0.12976	165.83	0.42859	271.93	0.92197	60.41
0.14456	179.02	0.52567	258.28	0.94240	44.95
0.15244	185.50	0.62417	228.11	0.97276	21.11

x	H_m^E / J mol^{-1}	x	H_m^E / J mol^{-1}	x	H_m^E / J mol^{-1}
$(1-x)$acetonitrile + x DMSO					
0.01104	3.07	0.25483	36.77	0.75833	11.97
0.02190	5.49	0.33120	37.10	0.82232	8.09
0.06219	14.29	0.35647	37.71	0.82957	7.48
0.08261	17.98	0.35699	37.68	0.90086	2.76
0.11710	24.54	0.44616	35.76	0.94612	0.882
0.11787	23.41	0.56361	29.43	0.98799	-0.051
0.17977	31.87	0.65566	20.93	0.99860	-0.040
0.25469	36.74	0.74491	13.71		
$(1-x)$propionitrile + x DMSO					
0.01981	35.39	0.42445	400.099	0.77848	273.25
0.04634	80.40	0.49249	406.22	0.79864	254.50
0.08061	130.35	0.51958	401.02	0.86308	184.85
0.11365	177.13	0.58056	393.14	0.89358	148.93
0.13985	210.89	0.62432	374.42	0.92670	106.67
0.22667	297.28	0.70856	325.00	0.95927	59.77
0.31899	362.65	0.71557	323.72	0.97795	34.09
$(1-x)$butyronitrile + x DMSO					
0.01466	32.90	0.18804	328.39	0.75332	417.96
0.02863	61.01	0.26844	427.25	0.81390	340.66
0.05282	109.71	0.36168	496.49	0.88572	239.91
0.06162	128.41	0.48241	546.97	0.92798	154.83
0.10048	197.69	0.56833	532.76	0.94422	125.80
0.12283	234.66	0.66563	497.14	0.97960	49.72
$(1-x)$pentanenitrile + x DMSO					
0.01000	27.48	0.26317	527.88	0.78477	522.33
0.03680	95.96	0.30353	579.30	0.84839	410.23
0.06874	170.41	0.40905	668.21	0.90502	281.98
0.11955	281.67	0.52390	708.11	0.92700	225.36
0.17092	383.66	0.60972	691.74	0.94899	161.91
0.20168	440.13	0.73497	589.38	0.97594	81.15
$(1-x)$benzonitrile + x DMSO					
0.02507	27.12	0.33284	210.53	0.7815	156.28
0.05460	54.12	0.41672	229.113	0.8377	124.20
0.11203	100.17	0.43773	230.653	0.8969	83.47
0.14865	129.39	0.45008	231.193	0.8990	82.07
0.18897	151.18	0.52749	233.123	0.9326	58.13
0.18973	151.22	0.53040	231.96	0.9669	28.17
0.23062	172.84	0.60491	221.08	0.9865	11.11
0.29625	199.12	0.66317	205.98		
0.31575	206.02	0.73452	179.40		

calorimetric procedures and reproducibility test of this calorimeter system were described elsewhere.[2,4,14,15)]

3. Results and Discussion

The experimental results of excess enthalpies obtained are summarized in **Table 1** and plotted in **Fig.1** and **Fig.2**. All the excess enthalpies of nitriles + MMTSO observed were positive over the whole range of mole fractions at 298.15 K. Excess enthalpies of mixtures for nitriles + MMTSO and + DMSO were fitted with Eqn.(1) by the method of least squares, and are described as solid lines in **Fig.1** and **Fig.2**.

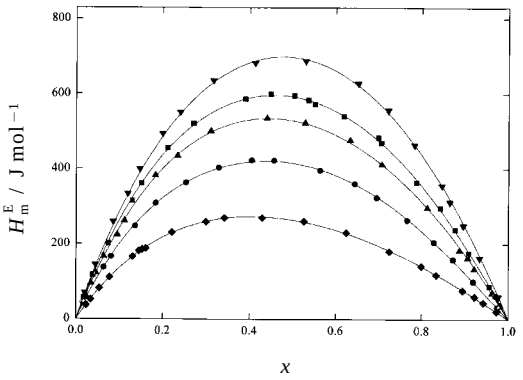

Fig.1 Excess enthalpies of mixing at 298.15 K. ●; (1 − *x*)acetonitrile + *x*MMTSO, ▲; (1 − *x*)propionitrile + *x*MMTSO, ■; (1 − *x*)butyronitrile + *x*MMTSO, ▼; (1 − *x*)pentanenitrile + *x*MMTSO, ◆; (1 − *x*)benzonitrile + xMMTSO.

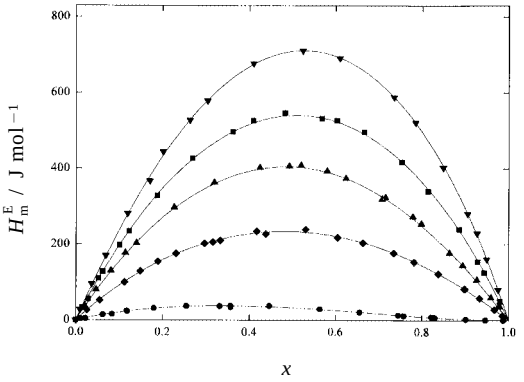

Fig.2 Excess enthalpies of mixing at 298.15 K. ●; (1 − *x*)acetonitrile + *x*DMSO, ▲; (1 − *x*)propionitrile + *x*DMSO, ■; (1 − *x*)butyronitrile + *x*DMSO, ▼; (1 − *x*)pentanenitrile + *x*DMSO, ◆; (1 − *x*)butyronitrile + *x*DMSO.

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

$$s_f/\mathrm{J\ mol^{-1}} = \left[\sum_{i=1}^{n}\{H^E_{m,i}(\mathrm{obs.}) - H^E_{m,i}(\mathrm{calc.})\}^2/(n-k)\right]^{1/2} \quad (2)$$

The coefficients A_i in Eqn.(1) and standard deviations of the fits s_f are given in **Table 2**. The excess enthalpies of nitriles + MMSTO were increased with increasing size of aliphatic groups of aliphatic nitriles as the mixtures of alkane-1-ol + MMTSO [5] and alkane-1-amine + MMTSO.[13] The mixtures of benzonitrile + MMTSO and pentanenitrile + MMTSO showed the smallest and the largest excess enthalpies among the mixtures of nitriles + MMTSO, respectively.

Table 2 Best-fit values for the coefficients A_i of Eqn.(1) and the calculated standard deviations of the fit s_f.

System	A_1	A_2	A_3	A_4	s_f / J mol^{-1}
acetonitrile + MMTSO	1661.8	360.6	224.0	282.7	1.3
propionitrile + MMTSO	2116.7	421.6	317.7	101.7	0.8
butyronitrile + MMTSO	2372.0	365.9	298.3	184.5	1.9
pentanenitrile + MMTSO	2793.2	232.1	273.2	82.8	1.0
benzonitrile + MMTSO	1051.1	385.0	196.3	67.7	0.9
acetonitrile + DMSO	132.0	115.2	2.0	23.1	0.5
propionitrile + DMSO	1618.5	99.2	6.6	42.2	1.2
butyronitrile + DMSO	2162.4	−75.0	179.1	−37.1	3.2
pentanenitrile + DMSO	2815.3	−312.8	290.9	−57.5	1.1
benzonitrile + DMSO	932.4	11.4	53.4	114.9	1.1

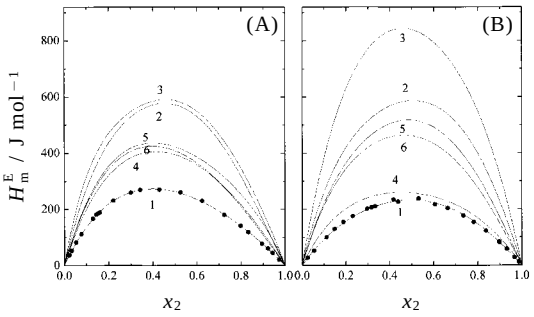

Fig.3 Excess enthalpies at 298.15 K. (A); (1 − *x*)aromatic compounds + *x*MMTSO. (B); (1 − *x*)aromatic compounds + *x*DMSO. 1; benzonitrile, 2; benzene, 3; toluene, 4; fluorobenzene, 5; chlorobenzene, 6; bromobenzene.

Comparing the excess enthalpies of benzonitrile + MMTSO with those of benzene and monosubstituted benzenes + MMTSO[2,6,9] in **Fig.3(A)**, the mixture of toluene + MMTSO showed the largest enthalpic unstabilization on mixing among those of aromatic compounds + MMTSO. The sequence of excess enthalpies of aromatic + MMTSO at their maxima is Toluene >

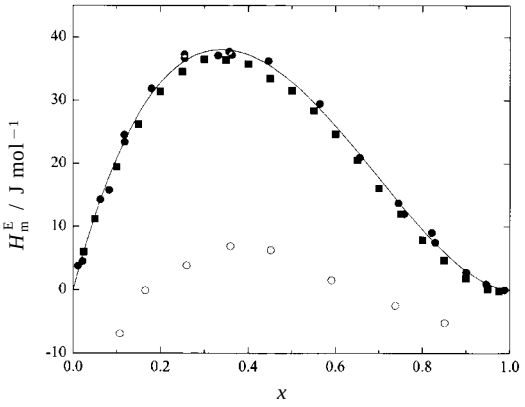

Fig.4 Excess enthalpies of mixing of $(1-x)$acetonitrile + xDMSO at 298.15 K. ●; this work, ■; Nakamura *et al.*,[16] ○; results obtained with wet acetonitrile (water content is 1 per cent).

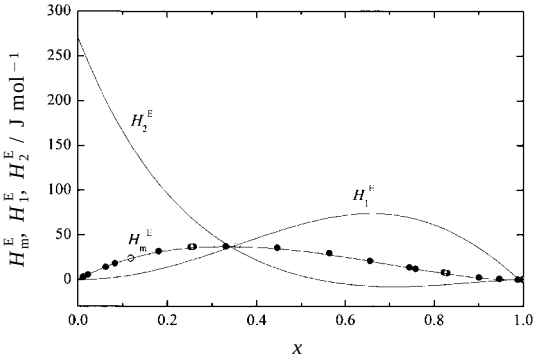

Fig.5 Excess enthalpies of mixing and excess partial molar enthalpies of acetonitrile(1) + DMSO(2) at 298.15 K.

benzene > chlorobenzene > bromobenzene > fluorobenzene > benzonitrile.

The system of benzonitrile + MMTSO showed the smallest enthalpic unstabilization among the aromatic compounds + MMTSO as shown in **Fig.3(A)**. Large enthalpic stabilization of dipole-dipole interaction in each pure component might decrease on mixing. The enthalpic stabilization from induced dipole-dipole interaction between phenyl ring and the dipole of MMTSO might be reducing the unstabilization on mixing. Comparing the excess enthalpies of benzonitrile + DMSO with those of benzene and monosubstituted benzenes + DMSO[2,6,9] in **Fig.3(B)**, the mixtures of toluene + DMSO showed the largest enthalpic unstabilization on mixing among those of aromatic + DMSO as well as the systems containinig MMTSO. The sequence of enthalpies of aromatic + DMSO at their maxima is the same as those of aromatic + MMTSO. Those behavours of aromomatic compounds + DMSO were very similar as aromomatic compounds + MMTSO as shown in **Fig.3(B)**.

All the excess enthalpies of nitriles + DMSO observed were positive over the whole range of mole fractions at this temperature except the mixtures of acetonitrile + DMSO over 0.95 in mole fraction of DMSO as showed in **Fig.2**. Excess enthalpies of nitrile compounds + DMSO showed almost similar effect on the substitution with aliphatic and phenyl groups as those of nitriles + MMTSO. The excess enthalpies of acetonitrile + DMSO were reported by Nakamura *et al.*[16] and Christensen et al.[17] The results of Nakanura et al. are also plotted in **Fig.4** for comparison. However, results of Christensen *et al.*[17] of the system showed different sigh of excess enthalpies and 5 times smaller values than this work. In order to evaluate effect of water content on excess enthalpies, the excess enthalpies using acetonitrile containing one per cent water were measured and plotted in **Fig.4**. As shown in **Fig.4**, the excess enthalpies were 20 J mol^{-1} to 30 J mol^{-1} smaller than the results which water content were less than 0.01 mole per cent.

Excess partial molar enthalpies of acetonitirle + DMSO were determined from Eqn.(1) with the coefficients listed in **Table 2** and are plotted in **Fig.5**. Excess partial molar enthalpy of acetonitrile and DMSO showed a maximum and a minimum at 0.68 in mole fraction of DMSO, respectively. Excess partial molar enthalpies of DMSO $H_2^{E,\infty}$ showed negative over the mole fraction of 0.55 even excess enthalpies of mixing were positive over the whole range of mole fraction. DMSO in liquid state is reported to be rigid clustering state[18] and also acetonitrile molecules in liquid state is considered to be order by strong anitiparallel pair interaction by through X-ray analysis.[19] Those results showed that stabilization in enthalpy by addition of DMSO into the mixture slightly increases with decrease in mole fraction of DMSO until the H_2^E reach the minimum in DMSO rich region. These results may be explained that the strength of dipole-dipole interaction between acetonitrile molecules and DMSO is

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}
acetonitrile(1)+MMTSO(2)	1.24	2.53
propionitrile(1)+MMTSO(2)	1.91	2.96
butyronitrile(1)+MMTSO(2)	2.12	3.22
pentanenitrile(1)+MMTSO(2)	2.71	3.59
benzonitrile(1)+MMTSO(2)	0.79	1.70
acetonitrile(1)+DMSO(2)	−0.004	0.27
propionitrile(1)+DMSO(2)	1.55	1.84
butyronitrile(1)+DMSO(2)	2.45	2.23
pentanenitrile(1)+DMSO(2)	3.48	2.74
benzonitrile(1)+DMSO(2)	0.86	1.11

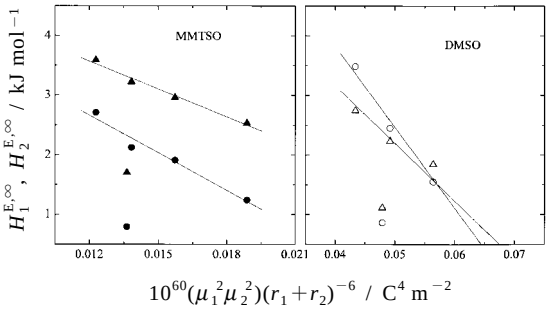

Fig.6 Correlation between the limiting partial molar excess enthalpies and $(\mu_1^2\mu_2^2)(r_1+r_2)^{-6}$. ●; $H_1^{E,\infty}$ (MMTSO), ▲; $H_2^{E,\infty}$ (MMTSO), ○; $H_1^{E,\infty}$ (DMSO), △; $H_2^{E,\infty}$ (DMSO).

much stronger than those between acetonitrile molecules.

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies at infinite dilutions were determined from Eqn.(1) with the coefficients in **Table 2**, and summarized in **Table 3**. The limiting excess partial molar enthalpies of aliphatic nitrile+MMTSO and, aliphatic nitrile+DMSO were increased with increasing the size of alkyl groups. The limiting excess partial molar enthalpies of the nitriles $H_1^{E,\infty}$ of all the mixtures with MMTSO or DMSO studied were smaller than those of MMTSO or DMSO $H_2^{E,\infty}$, respectively except the mixtures of butyronitrile and pentanenitrile+DMSO. 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] alkane-1-ols[5] and alkane-1-amines[13] were different. The limiting excess partial molar enthalpies of the MMTSO were larger than those of DMSO for all nitrile, which measured. There are dipole-dipole interaction effects and dipole-induced dipole interaction effects on the limiting excess partial molar enthalpies of the mixtures between nitriles+sulfides. The dipole-dipole interaction energy u_{12}(d-d) is expressed as an equation;[20]

$$u_{12}(\text{d-d}) = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{r^6\,kT} \qquad (3)$$

The values of $H_1^{E,\infty}$ and $H_2^{E,\infty}$ are plotted against squares of dipole moments μ divided with sextruplocate of distance between nitriles and sulfoxides. As zero-th estimation, r^6 was aproximated to $(r_1+r_2)^6$. Here r_1 and r_2 are radius as the sphere molecule of nitriles and sulfoxides, respectively. Linear relationships were obtained as shown in **Fig.6** between the limiting excess partial molar enthalpies of the mixtures of nitriles+MMTSO and +DMSO except the mixtures of benzonitrile. The coefficients of Eqn.(4) and the standard deviations are listed in **Table 4**.

Table 4 Best fit values for the coefficients of eqn.(4).

System	$H_i^{E,\infty}$	$a_{d\text{-}d}$ / kJ mol^{-1}	$10^{60}b_{d\text{-}d}$ / kJ mol^{-1} C^{-4} m^2	s_f / J mol^{-1}
nitriles+MMTSO	$H_1^{E,\infty}$	5.18	−210.0	0.13
	$H_2^{E,\infty}$	5.44	−155.7	0.07
nitriles+DMSO	$H_1^{E,\infty}$	9.26	−135.6	0.12
	$H_2^{E,\infty}$	7.03	−96.60	0.22

$$H_i^{E,\infty}/\text{kJ mol}^{-1} = a_{d\text{-}d} + b_{d\text{-}d}\ \mu_1^2\mu_2^2(r_1+r_2)^{-6} \qquad (4)$$

μ_i; dipole moment of component i.

r_i; radius as the sphere molecule of component i.

Enthalpic unstabilization of aliphatic nitriles+sulfoxide were decreased with increasing stabilization of dipole-dipole interaction between aliphatic nitrile and sulfoxide. The stabilization of dipole-dipole interactions might be a major interaction of those systems.

Those partial molar enthalpies of the mixtures contained benzonitrile in **Fig.6** were less destabilized at infinite dilution compared with other nitriles. It might be a dipole-induced dipole interaction between phenyl group of benzonitrile and sulfoxides.

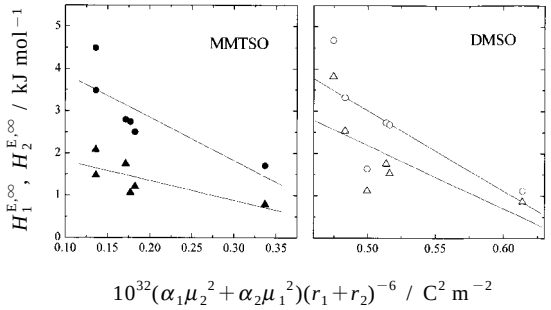

Fig.7 Correlation between the limiting partial molar excess enthalpies $H_1^{E,\infty}$ and $(\alpha_2\mu_1^2+\alpha_1\mu_2^2)$ $(r_1+r_2)^{-6}$. ●; $H_1^{E,\infty}$ (MMTSO), ▲; $H_2^{E,\infty}$ (MMTSO), ○; $H_1^{E,\infty}$ (DSMO), △; $H_2^{E,\infty}$ (DMSO).

Table 5 Best values for the coefficients of Eqn.(6).

System	$H_i^{E,\infty}$	$a_{d\text{-}id}$ / kJ mol^{-1}	$10^{30}b_{d\text{-}id}$ / kJ mol^{-1} C^2 m^{-1}	$10^{30}s_f$ / kJ mol^{-1} C^2 m^{-1}
aromatic compounds(1)+MMTSO(2)				
	$H_1^{E,\infty}$	2.28	−468	0.35
	$H_2^{E,\infty}$	4.89	−1025	0.62
aromatic compounds(2)+DMSO(2)				
	$H_1^{E,\infty}$	9.68	−1497	0.88
	$H_2^{E,\infty}$	12.5	−1899	0.92

A dipole-induced dipole interaction energy u_{12}(d-id) is expressed as an equation;[20]

$$u_{12}(\text{d-id}) = -\frac{\alpha_2\mu_1^2+\alpha_1\mu_2^2}{r^6} \quad (5)$$

The values of $H_1^{E,\infty}$ and $H_2^{E,\infty}$ of aromatic compounds (benzene, toluene, fluorobenzene, chlorobenzene and bromobenzene)[2,6,9] are plotted against sum of the product of polarizability and squares of dipole moments divided with r^6 of components[21,22] for the sake of understanding the effect on dipole-induced dipole interaction. Linear relationships were obtained as shown in **Fig.7** between the limiting excess partial molar enthalpies of the mixtures of aromatic compounds+MMTSO and +DMSO except the system of tolunene+MMTSO and +DMSO. The coefficients of Eqn.(6) and the standard deviations are listed in **Table 5**.

$$H_i^{E,\infty}/\text{kJ mol}^{-1} = a_{d\text{-}id}+b_{d\text{-}id}(\alpha_2\mu_1^2+\alpha_1\mu_2^2)(r_1+r_2)^{-6} \quad (6)$$

μ_i, α_i, r_i are dipole moment, polarizability and radius as the sphere molecule of component i, respectively.

Excess partial molar enthalpies at infinite dilution of the mixtures containing MMTSO or DMSO were decreased with increasing the interaction energy due to dipole-induced dipole interaction. The values of enthalpic stabilization of aromatic compounds+MMTSO or +DMSO and dipole-induced dipole interaction energies have good linearity for the observed mixtures of aromatic compounds+MMTSO and +DMSO. Furthermore, the effect of dipole-induced dipole interaction on excess partial molar enthalpies at infinite dilution of the mixtures containing bd-id in Eqn.(7), were smaller than those containing DMSO. Because DMSO molecules (dipole moment: 13.4×10^{-30} cm)[23] have larger dipolar stabilization than MMTSO molecules (10.7×10^{-30} cm)[21] in pure liquid state.

It was explained that the major effect on the excess enthalpies of solvent+MMTSO and +DMSO might arise from hindering of stable dipolar or induced dipolar contacts by the less polar components. However, the mixtures of nitriles+MMTSO and +DMSO have not only same effect as non-polar solvent reported previously[6] but also additional, relatively large energetic effect from dipole-dipole interaction and dipole-induced dipole interaction.

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要　旨

アセトニトリル，プロピオニトリル，ブチロニトリル，ペンタンニトリルおよびベンゾニトリル+メチルメチルチオメチルスルホキシド（MMTSO）あるいはジメチルスルホキシド（DMSO）との混合エンタルピーを298.15 Kで測定した。測定した混合エンタルピーはアセトニトリル+DMSO系の0.95以上の濃度を除いてすべて吸熱系であった。

アセトニトリル(1)＋DMSO (2) 系のモル分率0.65付近に部分モルエンタルピーH_1^Eの極大とH_2^Eの極小が見出された。ベンゾニトリル系を除いて $(\mu_1^2\mu_2^2)(r_1+r_2)^{-6}$と部分モルエンタルピーはよい相関を示した。また芳香族化合物系の部分モルエンタルピーは $(\alpha_2\mu_1^2+\alpha_1\mu_2^2)(r_1+r_2)^{-6}$とよい相関を示した。

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