Excess Enthalpies of {$CH_3(CH_2)_nCN$, n = 5 to 12} + Methyl Methylthiomethyl Sulfoxide or + Dimethyl Sulfoxide at 298.15 K

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Excess enthalpies of binary mixtures between each of {$CH_3(CH_2)_nCN$ (n = 5−12)} and methyl methylthiomethyl sulfoxide or dimethyl sulfoxide have been determined at 298.15 K. All mixtures show positive enthalpy changes over the whole range of mole fractions. Excess enthalpies of the mixtures of nitriles increased with increasing size of the aliphatic groups. The increments of dipole interaction terms of $\mu_1^2\mu_2^2(r_1 + r_2)^{-6}$ on excess partial molar enthalpies at infinite dilution showed different behavior on the border of pentanenitrile.

1. Introduction

In our previous papers,[1−16] excess thermodynamic functions for the binary mixtures of methyl methylthiomethyl sulfoxide (MMTSO) with water, benzene, dimethyl sulfoxide (DMSO), carbon tetrachloride, chloroform, dichloromethane, deuteriochloroform, *n*-alkane-1-ols ($C_nH_{2n+1}OH$, n = 1 to 4), six methyl-benzenes {$C_6H_{6-n}(CH_3)_n$, n = 1 to 3}, six cycloethers, three aliphatic-ethers, aliphatic benzene {$C_6H_5(CH_2)_nCH_3$, n = 0 to 7}, five monohalogenated aromatic compounds (benzene and toluene), six *o*- and *m*-dihalogenated benzenes, aliphatic amine {$C_nH_{2n+1}NH_2$, n = 3 to n = 8}, some nitrile (acetonitrile, propionitrile, butyronitrile, pentanenitrile, benzonitrile), and DMSO were reported.

To know further information between 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 nitrile {$CH_3(CH_2)_nCN$, n = 5−12} were determined over the whole range of mole fractions. Those of nitriles + DMSO were also determined as the reference systems.

2. Experimental Section

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] {$CH_3(CH_2)_nCN$, n = 5−12 (Tokyo kassei, 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. Gas−liquid chromatography results obtained by using each 2-m column of 10% SE-30 on chromosorb and 20% PEG-1000 on Celite 545 with a flame ionization detector on Yanagimoto G180FP showed merely some trace impurity peaks ($<10^{-7}$). Karl Fischer's coulometric method on a Moisturemeter (Mitsubishi Chemical Ind., CA-02) gave the water content of each sample to be 0.01 mole percent or less.

Apparatus and Procedures. A twin microcalorimeter of the heat-conduction type (Larkin-MacGlashan type, laboratory designation MC-AII) was used for measurements of excess enthalpies at 298.15 K over the whole range of mole fractions. The details and modification of calorimetric procedures of the batch calorimeter[2,4,16] and the reproducibility test of the calorimeter were already reported with the results of (cyclohexane + hexane),[17] (benzene + carbon tetrachloride),[18] (chlorobenzene + toluene),[17] (1,4-dimethylbenzene + 1,3-dimethylbenzene),[19] and (1,4-dimethylbenzene + 1,2-dimethylbenzene)[19] at 298.15 K. The results were in excellent agreement with those of reported values within 0.2%.

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3. Results and Discussion

The experimental results of excess enthalpies obtained are summarized in Table 1. The excess enthalpies were fitted to a Redlich−Kister-type equation (eq 1) by a method of least squares

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

The coefficients A_i in eq 1 and standard deviations of the fits s_f

$$s_f = [\sum_{i=1}^{n} \{H^E(\mathrm{exp}) - H^E(\mathrm{calc})\}_i^2/(n - k)]^{1/2} \qquad (2)$$

are given in Table 2. Excess enthalpies of nitriles + MMTSO or DMSO were plotted in Figures 1 and 2 with previously reported results.[15] All the excess enthalpies of nitriles + MMTSO observed were positive over the whole range of mole fractions at this temperature. The excess enthalpies of nitriles + MMTSO were increased with increasing size of aliphatic groups of aliphatic nitriles as the mixtures of *n*-alkane-1-ol + MMTSO[5] and aliphatic amines + MMTSO.[13] 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 nitriles. However, the excess enthalpies of nitriles{$CH_3(CH_2)_nCN$, n = 10−12} + MMTSO did not show the same behavior as

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Table 1. Excess Enthalpies of $(1 - x)C_nH_{2n+1}CN + x$MMTSO and $+ x$DMSO at 298.15 K

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
					$(1 - x)C_5H_{11}CN + x$MMTSO						
0.01678	54.23	0.07605	246.61	0.21844	590.92	0.43816	807.47	0.73069	628.00	0.93924	195.82
0.02979	103.53	0.14347	432.66	0.26080	660.31	0.47847	811.15	0.83732	449.27	0.97844	74.47
0.05841	197.29	0.19443	545.47	0.38263	787.11	0.57507	782.80	0.91768	254.91		
					$(1 - x)C_6H_{13}CN + x$MMTSO						
0.02045	81.779	0.09776	357.47	0.27014	741.81	0.57903	885.16	0.86087	465.84	0.95755	165.36
0.05221	200.79	0.19348	599.17	0.38932	869.91	0.74778	714.35	0.93596	247.39	0.97141	115.26
0.08567	318.76	0.22081	655.24	0.49145	902.28						
					$(1 - x)C_7H_{15}CN + x$MMTSO						
0.02232	86.90	0.16005	557.95	0.52073	991.67	0.77689	741.67	0.91289	367.26	0.95479	207.85
0.06732	267.86	0.22318	709.33	0.62178	952.17	0.86897	509.42	0.92657	323.81	0.98789	64.63
0.10826	404.73	0.34762	905.51	0.70864	861.90						
					$(1 - x)C_8H_{17}CN + x$MMTSO						
0.01839	83.26	0.11857	453.92	0.26856	830.53	0.46544	1044.0	0.77903	815.18	0.90583	442.49
0.03954	172.05	0.17500	624.33	0.37211	970.20	0.55644	1059.1	0.84168	650.21	0.95644	222.26
0.08357	335.24	0.22570	744.10	0.38121	980.75	0.64093	1009.6	0.88056	527.63	0.97840	111.19
					$(1 - x)C_9H_{19}CN + x$MMTSO						
0.02311	95.42	0.10586	450.91	0.22775	851.45	0.49346	1137.9	0.74821	919.17	0.97599	147.15
0.02808	121.43	0.12671	535.29	0.28933	971.07	0.55715	1125.3	0.78729	839.35	0.98803	80.65
0.05736	248.93	0.15155	621.75	0.33825	1049.6	0.65753	1049.0	0.86093	659.24		
0.07887	338.15	0.18600	735.78	0.36567	1082.0	0.70139	998.61	0.94677	304.60		
					$(1 - x)C_{10}H_{21}CN + x$MMTSO						
0.02536	121.39	0.07724	362.93	0.18890	758.75	0.42181	1164.88	0.86944	712.58	0.99330	54.76
0.04055	193.83	0.12169	532.07	0.26285	934.23	0.50518	1198.36	0.90428	579.11		
0.04193	207.48	0.14017	593.45	0.27667	967.71	0.76998	990.59	0.90950	550.30		
0.07582	358.34	0.15961	663.42	0.32337	1055.91	0.83161	843.64	0.94642	361.33		
					$(1 - x)C_{11}H_{23}CN + x$MMTSO						
0.03008	156.92	0.10079	476.39	0.21522	853.47	0.50237	1256.9	0.81155	934.03	0.98647	99.50
0.03781	199.17	0.17895	745.83	0.31974	1090.7	0.58571	1261.1	0.89791	619.17		
0.09203	447.54	0.20702	826.39	0.35167	1131.3	0.70835	1158.3	0.95923	279.17		
					$(1 - x)C_{12}H_{25}CN + x$MMTSO						
0.06513	322.92	0.20136	873.19	0.36704	1207.7	0.63440	1231.5	0.80393	948.42	0.98468	122.54
0.08230	433.31	0.26496	1037.3	0.42330	1260.1	0.73408	1106.4	0.90824	578.13		
0.13165	629.07	0.35085	1178.4	0.54426	1279.9	0.78781	991.81	0.96829	245.87		
					$(1 - x)C_{13}H_{27}CN + x$MMTSO						
0.03538	172.50	0.12886	638.19	0.33483	1176.4	0.67208	1185.4	0.88669	718.75	0.95664	364.58
0.05372	288.19	0.15650	740.97	0.50497	1270.1	0.81550	956.25	0.91235	605.04	0.98583	147.16
0.08438	431.94	0.19838	879.86	0.63321	1216.8						
					$(1 - x)C_5H_{11}CN + x$DMSO						
0.07452	228.27	0.19522	524.31	0.35280	772.60	0.58063	858.82	0.84202	541.02	0.95592	190.01
0.09271	278.41	0.25833	645.47	0.43434	840.04	0.71543	758.58	0.88923	411.73	0.98554	62.33
0.14739	418.67	0.31349	727.24	0.49079	865.11						
					$(1 - x)C_6H_{13}CN + x$DMSO						
0.02225	65.48	0.11901	341.07	0.22484	595.24	0.35810	834.02	0.57721	975.09	0.89461	476.61
0.07063	209.52	0.17473	483.93	0.24226	639.88	0.36048	842.86	0.65219	946.90	0.95454	229.73
0.08316	247.02	0.18510	516.07	0.30490	750.25	0.49352	962.50	0.70562	896.43	0.97925	111.69
					$(1 - x)C_7H_{15}CN + x$DMSO						
0.02667	81.39	0.17998	558.78	0.38769	976.24	0.62328	1072.4	0.87848	622.46	0.99199	56.390
0.03700	122.69	0.23991	707.76	0.46544	1048.5	0.70216	1019.4	0.95457	284.31		
0.11760	373.09	0.32928	889.42	0.55198	1090.7	0.82670	789.80	0.96158	238.31		
					$(1 - x)C_8H_{17}CN + x$DMSO						
0.05896	214.05	0.17214	589.58	0.26976	852.21	0.54248	1191.5	0.77343	1026.3	0.97120	222.23
0.07322	260.71	0.18985	638.23	0.28359	882.74	0.54423	1192.5	0.84959	825.78	0.99172	70.980
0.09784	345.54	0.23650	764.71	0.38409	1054.6	0.55688	1193.0	0.89909	627.91		
0.12851	448.96	0.24082	783.78	0.45767	1138. 9	0.70302	1134.7	0.93900	430.05		
					$(1 - x)C_9H_{19}CN + x$DMSO						
0.03778	141.51	0.14578	553.25	0.23200	816.28	0.54708	1263.1	0.79786	1051.4	0.96202	320.11
0.04533	174.88	0.15156	571.60	0.34924	1072.9	0.55644	1270.0	0.92118	582.52	0.98675	123.34
0.07244	270.13	0.15778	591.70	0.44044	1192.0	0.62527	1261.1				
0.08356	312.07	0.21378	767.34	0.52000	1250.9	0.72750	1180.6				
					$(-x)C_{10}H_{21}CN + x$DMSO						
0.02797	120.26	0.12073	499.68	0.28546	1042.4	0.53020	1348.2	0.82916	1062.6	0.97725	228.84
0.05445	229.28	0.18110	731.13	0.39240	1238.1	0.64232	1347.6	0.89166	816.93	0.98002	205.49
0.09234	391.81	0.18531	743.30	0.51391	1347.0	0.71615	1287.4	0.92981	607.51	0.99269	80.03
					$(1-x)C_{11}H_{23}CN + x$DMSO						
0.02506	96.81	0.09988	434.10	0.19476	811.73	0.43079	1366.4	0.86020	965.65	0.96487	334.82
0.02612	109.08	0.16647	701.95	0.25217	1017.1	0.56199	1425.9	0.89559	805.55	0.98859	120.16
0.07491	319.77	0.17912	772.39	0.33663	1224.1	0.75923	1248.5	0.94610	478.28		

Table 1 (Continued)

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
					$(1-x)C_{12}H_{25}CN + x$DMSO						
0.02177	82.540	0.22021	884.30	0.42317	1292.3	0.77528	1182.5	0.92857	601.59	0.98207	191.99
0.06754	285.71	0.25754	989.68	0.54641	1345.8	0.80335	1125.2	0.95707	401.0	0.09988	434.10
0.09519	398.41	0.27092	1019.1	0.63580	1330.2	0.86087	946.56				
0.12290	518.55	0.27999	1057.1	0.73944	1243.7	0.90007	758.73				
					$(1-x)C_{13}H_{27}CN + x$DMSO						
0.02407	128.45	0.14146	642.30	0.30633	1165.5	0.61857	1442.5	0.89619	839.68	0.96916	331.75
0.06045	280.75	0.21933	916.76	0.41814	1351.2	0.76189	1299.2	0.91096	736.09	0.98093	205.36
0.12189	558.52	0.25268	1018.9	0.48769	1419.1	0.87157	959.52	0.95318	454.76		

Table 2. Best-Fit Values for the Coefficients A_i of Equation 1 with the Standard Deviations of the Fit s_f

system	A_1	A_2	A_3	A_4	s_f/J·mol^{-1}
$(1-x)CH_3CN + x$MMTSO[15]	1661.8	360.6	224.0	282.7	1.3
$(1-x)C_2H_5CN + x$MMTSO[15]	2116.7	421.6	317.7	101.7	0.8
$(1-x)C_3H_7CN + x$MMTSO[15]	2372.0	365.9	298.3	184.5	1.9
$(1-x)C_4H_9CN + x$MMTSO[15]	2793.2	232.1	273.2	82.8	1.0
$(1-x)C_5H_{11}CN + x$MMTSO	3239.5	313.6	329.6	−328.0	1.9
$(1-x)C_6H_{13}CN + x$MMTSO	3620.5	3.4	606.0	15.8	3.0
$(1-x)C_7H_{15}CN + x$MMTSO	3975.5	−115.1	675.7	−212.3	3.7
$(1-x)C_8H_{17}CN + x$MMTSO	4218.4	−394.8	843.6	−74.1	3.6
$(1-x)C_9H_{19}CN + x$MMTSO	4565.0	209.8	1087.1	−1279.1	5.7
$(1-x)C_{10}H_{21}CN + x$MMTSO	4788.8	−395.5	1581.7	−931.4	4.4
$(1-x)C_{11}H_{23}CN + x$MMTSO	5036.8	−669.9	1485.8	−390.0	4.9
$(1-x)C_{12}H_{25}CN + x$MMTSO	5125.3	−112.2	1678.7	−1094.9	7.2
$(1-x)C_{13}H_{27}CN + x$MMTSO	5075.7	152.5	2229.5	−1947.5	6.0
$(1-x)CH_3CN + x$DMSO[15]	132.0	115.2	2.0	23.1	0.5
$(1-x)C_2H_5CN + x$DMSO[15]	1618.5	99.2	6.6	42.2	1.2
$(1-x)C_3H_7CN + x$DMSO[15]	2162.4	−75.0	179.1	−37.1	3.2
$(1-x)C_4H_9CN + x$DMSO[15]	2815.3	−312.8	290.9	−57.5	1.1
$(1-x)C_5H_{11}CN + x$DMSO	3459.2	−354.1	495.6	−355.3	1.9
$(1-x)C_6H_{13}CN + x$DMSO	3854.1	−872.2	462.7	−414.7	3.1
$(1-x)C_7H_{15}CN + x$DMSO	4290.2	−941.2	788.2	−924.5	3.3
$(1-x)C_8H_{17}CN + x$DMSO	4689.1	−1122.8	1205.6	−1213.4	3.3
$(1-x)C_9H_{19}CN + x$DMSO	4973.9	−1082.2	1584.7	−1717.1	4.8
$(1-x)C_{10}H_{21}CN + x$DMSO	5347.0	−999.7	2027.0	−2322.2	4.5
$(1-x)C_{11}H_{23}CN + x$DMSO	5655.4	−754.1	1652.1	−2585.8	5.8
$(1-x)C_{12}H_{25}CN + x$DMSO	5360.9	−688.1	1966.9	−2690.8	5.5
$(1-x)C_{13}H_{27}CN + x$DMSO	5691.1	−1131.5	2196.6	−2036.8	7.7

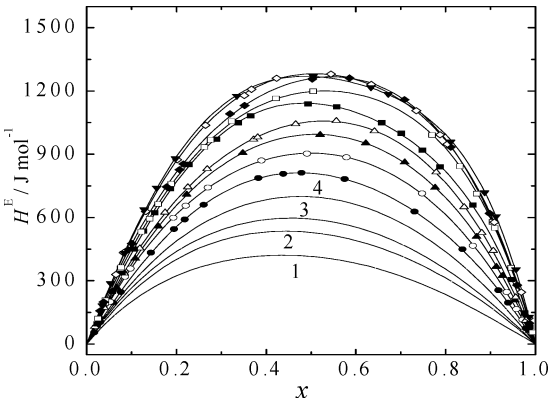

Figure 1. Excess enthalpies of $(1-x)C_nH_{2n+1}CN + x$MMTSO at 298.15 K: 1, $n = 1$; 2, $n = 2$; 3, $n = 3$; 4, $n = 4$; ●, $n = 5$; ○, $n = 6$; ▲, $n = 7$; △, $n = 8$; ■, $n = 9$; □, $n = 10$; ◆, $n = 11$; ◇, $n = 12$; ▼, $n = 13$.

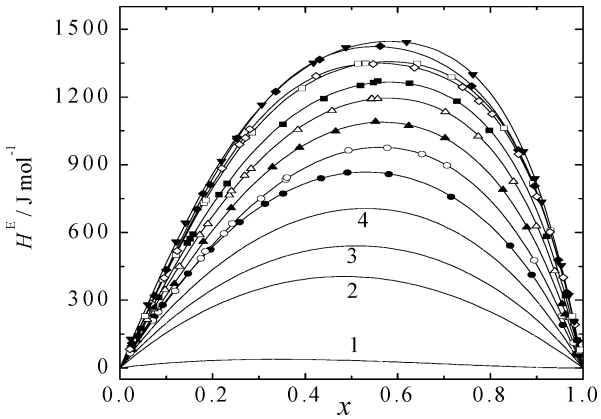

Figure 2. Excess enthalpies of $(1-x)C_nH_{2n+1}CN + x$DMSO at 298.15 K: 1, $n = 1$; 2, $n = 2$; 3, $n = 3$; 4, $n = 4$; ●, $n = 5$; ○, $n = 6$; ▲, $n = 7$; △, $n = 8$; ■, $n = 9$; □, $n = 10$; ◆, $n = 11$; ◇, $n = 12$; ▼, $n = 13$.

small nitriles{$CH_3(CH_2)_nCN$, $n = 0-9$}. The excess enthalpies of {$CH_3(CH_2)_nCN$, $n = 10-12$} + MMTSO were not increased with increasing size of aliphatic groups of aliphatic nitriles. Excess enthalpies of aliphatic nitrile compounds + DMSO observed were positive over the whole range of mole fractions at this temperature and showed a similar effect on the substitution with aliphatic groups as those of aliphatic nitrile + MMTSO as shown in Figure 2. Excess enthalpies of {$CH_3(CH_2)_nCN$, $n = 0-4$} + MMTSO were larger than those of {$CH_3(CH_2)_nCN$, $n = 0-4$} + DMSO, but excess enthalpies of {$CH_3(CH_2)_nCN$, $n = 5-12$} + MMTSO were less than those of {$CH_3(CH_2)_nCN$, $n = 5-12$} + DMSO, respectively. This size effect of aliphatic groups on excess enthalpies is different compared with all other mixtures that were measured for the system containing aliphatic alcohols, aliphatic benzene, and aliphatic amines.[5,13,15]

For the sake of an elementary consideration of pairwise interaction, excess partial molar enthalpies at infinite dilutions were determined from eq 1 with the coefficients in Table 2 and summarized in Table 3. Correlations between excess partial molar enthalpies at infinite dilution and the number of methylene groups were plotted in Figure

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}
$(1-x)CH_3CN + x$MMTSO[15]	1.24	2.53
$(1-x)C_2H_5CN + x$MMTSO[15]	1.91	2.96
$(1-x)C_3H_7CN + x$MMTSO[15]	2.12	3.22
$(1-x)C_4H_9CN + x$MMTSO[15]	2.75	3.38
$(1-x)C_5H_{11}CN + x$MMTSO	3.58	3.55
$(1-x)C_6H_{13}CN + x$MMTSO	4.21	4.25
$(1-x)C_7H_{15}CN + x$MMTSO	4.98	4.32
$(1-x)C_8H_{17}CN + x$MMTSO	5.53	4.59
$(1-x)C_9H_{19}CN + x$MMTSO	6.72	4.58
$(1-x)C_{10}H_{21}CN + x$MMTSO	7.70	5.04
$(1-x)C_{11}H_{23}CN + x$MMTSO	7.58	5.46
$(1-x)C_{12}H_{25}CN + x$MMTSO	8.01	5.60
$(1-x)C_{13}H_{27}CN + x$MMTSO	9.10	5.51
$(1-x)CH_3CN + x$DMSO[15]	−0.0043	0.272
$(1-x)C_2H_5CN + x$DMSO[15]	1.48	1.77
$(1-x)C_3H_7CN + x$DMSO[15]	2.45	2.23
$(1-x)C_4H_9CN + x$DMSO[16]	3.48	2.74
$(1-x)C_5H_{11}CN + x$DMSO	4.66	3.25
$(1-x)C_6H_{13}CN + x$DMSO	5.60	3.03
$(1-x)C_7H_{15}CN + x$DMSO	6.94	3.21
$(1-x)C_8H_{17}CN + x$DMSO	8.23	3.56
$(1-x)C_9H_{19}CN + x$DMSO	9.36	3.76
$(1-x)C_{10}H_{21}CN + x$DMSO	10.7	4.05
$(1-x)C_{11}H_{23}CN + x$DMSO	10.6	3.97
$(1-x)C_{12}H_{25}CN + x$DMSO	10.7	3.95
$(1-x)C_{13}H_{27}CN + x$DMSO	11.1	4.72

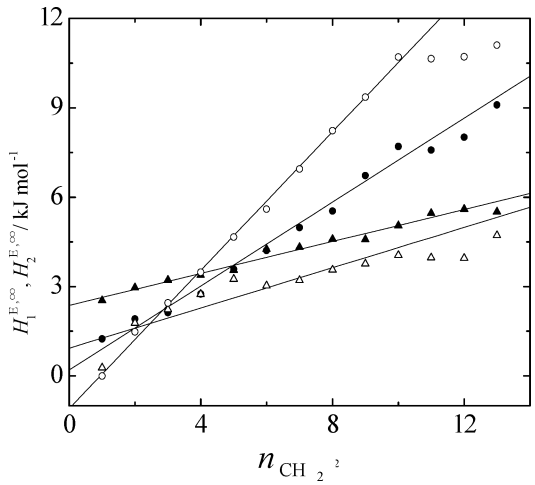

Figure 3. Correlation between excess partial molar enthalpies at infinite dilution and number of methylene group of aliphatic nitriles: ●, $H_1^{E,\infty}$(MMTSO)/kJ mol^{-1}; ▲, $H_2^{E,\infty}$(MMTSO)/kJ mol^{-1}; ○, $H_1^{E,\infty}$(DMSO)/kJ mol^{-1}; □, $H_2^{E,\infty}$(DMSO)/kJ mol^{-1}.

3. The excess partial molar enthalpies at infinite dilution of aliphatic nitriles + MMTSO and aliphatic nitriles + DMSO increased with increasing size of the aliphatic groups, except for $H_1^{E,\infty}$ of $\{CH_3(CH_2)_nCN$, $n = 10-12\}$ + MMTSO or +DMSO. The excess partial molar enthalpies at infinite dilution of nitrile $H_1^{E,\infty}$ of the aliphatic nitriles + MMTSO were larger than those of MMTSO $H_1^{E,\infty}$ for the mixtures containing nitriles $\{CH_3(CH_2)_nCN$, $n = 6-12\}$ but vice versa. The excess partial molar enthalpies at infinite dilution of aliphatic nitriles + DMSO were almost the same as those of aliphatic nitriles + MMTSO. The similar results of nitriles $\{CH_3(CH_2)_nCN$, $n = 6-12\}$ + MMTSO or DMSO were obtained for the mixtures of methylbenzenes, cycloethers, and aliphatic amines $\{C_nH_{2n+1}NH_2$, $n = 3-8\}$ + MMTSO,[6,7,14] although the mixtures of MMTSO with oxolane,[7] water,[2] chloromethanes,[3,4] and alkane-1-ols[5] were different. The excess partial molar enthalpies of nitriles at infinite dilution $H_1^{E,\infty}$ for aliphatic nitriles + DMSO were less unstable than for those of aliphatic nitriles + MMTSO for all mixture of aliphatic nitriles measured except the mixture containing acetonitrile and propionitrile. The hydrophobicity of the aliphatic nitrile may depend on the number of methylene groups in the aliphatic nitriles. Excess partial molar enthalpies at infinite dilution and the number of methylene groups are fitted with eq 3 by the method of least squares and are described as solid lines in Figure 3, and the best-fit coefficients of eq 3 were listed in Table 4

$$H_1^{E,\infty} = H_2^{E,\infty} = a_n + b_n n_c \tag{3}$$

Coefficient b_n in eq 3 might include the size effect of aliphatic groups on excess partial molar enthalpies. All coefficients b_n determined were positive and showed unfavorable interaction between sulfides and aliphatic groups of methylene. The size of the methylene group might induce the enhancement of unfavorable interaction between sulfides and aliphatic nitriles. Coefficients b_n of excess partial molar enthalpies of the mixtures of DMSO were larger than those of the mixtures of MMTSO. On the other hand, coefficients a_n in eq 3 might show the effect of nitrile groups on excess partial molar enthalpies. The coefficients a_n determined for nitriles + DMSO were negative and showed favorable interaction between sulfide and nitrile. But coefficients a_n of excess partial molar enthalpies of the mixtures of nitriles + MMTSO were positive and showed unfavorable interaction between sulfide and nitrile. The amphiphiles of aliphatic nitriles have two opposite interaction between sulfides. There might be not small dipole−dipole interaction effects on the limiting excess partial molar enthalpies of the mixtures between nitriles and sulfides. Interaction energy between molecules 1 and 2 were generally shown as eq 4

$$u = -\frac{m^2}{(4\pi\epsilon_0)^2 r^6}\left(\alpha 0 + \frac{\mu^2}{3kT}\right) \tag{4}$$

that for two different, nonpolarizable molecules takes the following form

$$u = -\frac{{\mu_1}^2}{(4\pi\epsilon_0)^2 r^6}\frac{{\mu_2}^2}{3kT} \tag{5}$$

because α_0 is zero. So u might be proportional as eq 6

$$u \propto \frac{{\mu_1}^2{\mu_2}^2}{r^6} \tag{6}$$

where μ, r, ϵ, and k are the dipole moment, distance

Table 4. Best Fit for the Coefficients of eq 3

a	a/J mol^{-1}	b_n/j mol^{-1}	s_f/J mol^{-1}	a	a/j mol^{-1}	b_n/J mol^{-1}	s_f/J mol^{-1}
	aliphatic nitriles(1) + MMTSO(2)				aliphatic nitriles(1) + DMSO(2)		
$H_1^{E,\infty}$	0.20	0.70	0.30	$H_1^{E,\infty}$	−1.10	1.16	0.16
$H_2^{E,\infty}$	2.37	0.27	0.15	$H_2^{E,\infty}$	0.93	0.34	0.48

[a] $H_i^{E,\infty} = a_n + b_n \cdot n\ n_{CH_2}$(3).

Table 5. Calculated Physical Properties of Aliphatic Nitriles and Sulfoxides

system	$10^{30}\ \mu^a$/C·m	10 V^a/nm^3	r^a/nm	system	$10^{30}\ \mu^a$/C·m	10 V^a/nm^3	r^a/nm
CH_3CN	9.65	2.20	0.374	$C_{10}H_{21}CN$	10.3	6.93	0.549
C_2H_5CN	9.80	2.76	0.404	$C_{11}H_{23}CN$	10.3	7.44	0.562
C_3H_7CN	10.0	3.30	0.429	$C_{12}H_{25}CN$	10.3	7.94	0.575
C_4H_9CN	10.1	3.80	0.449	$C_{13}H_{27}CN$	10.3	8.48	0.587
$C_5H_{11}CN$	10.2	4.31	0.469	MMTSO	8.17	4.00	0.457
$C_6H_{13}CN$	10.2	4.82	0.487	DMSO	13.16	2.92	0.412
$C_7H_{15}CN$	10.2	5.34	0.503	MMTSO[18]	10.7		
$C_8H_{17}CN$	10.3	5.88	0.520	DMSO[22]	13.4		
$C_9H_{19}CN$	10.3	6.42	0.535				

[a] μ is the dipole moment, V is the volume, and r is the radius.

Table 6. Best Fit for the Coefficients of Equation 5

system	n_{CH_2}	a	a_{dd}/kJ mol^{-1}	$10^{60}\ b_{dd}$/kJ mol^{-1}C^{-4}m^2	s_f/kJ mol^{-1}C^{-4}m^{-2}
aliphatic nitrile(1) + MMTSO(2)	1−4	$H_1^{E,\infty}$	5.27	−214	0.15
	5−13	$H_1^{E,\infty}$	13.6	−942	0.33
	1−4	$H_2^{E,\infty}$	5.00	−130	0.02
	5−13	$H_2^{E,\infty}$	7.62	−367	0.19
aliphatic nitrile(1) + DMSO(2)	1−4	$H_1^{E,\infty}$	9.25	−136	0.15
	5−13	$H_1^{E,\infty}$	18.6	−369	0.41
	1−4	$H_2^{E,\infty}$	7.03	−97.0	0.18
	5−13	$H_2^{E,\infty}$	5.13	−55	0.18

[a] $H_i^{E,\infty} = a_{dd} + b_{dd}(\mu_1^2\mu_2^2)(r_1 + r_2)^{-6}$.

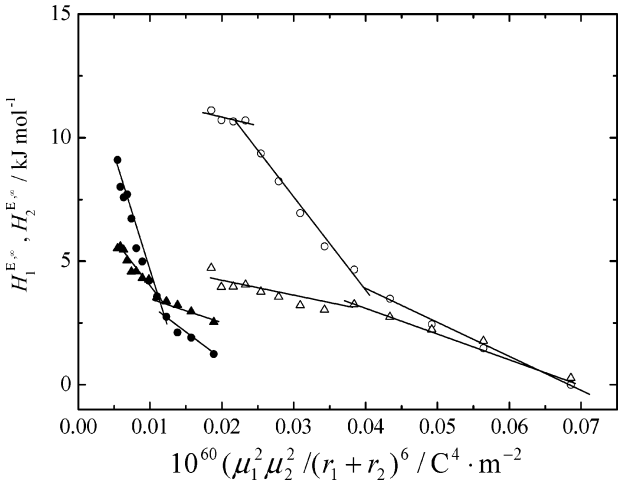

Figure 4. Correlation between excess partial molar enthalpies at infinite dilution and $\mu_1^2\mu_2^2(r_1 + r_2)^{-6}$ of aliphatic nitriles + MMTSO or + DMSO: ●, $H_1^{E,\infty}$(MMTSO); ▲, $H_2^{E,\infty}$(MMTSO); ○, $H_1^{E,\infty}$(DMSO); □, $H_2^{E,\infty}$(DMSO).

between molecules, dielectric constant, and Boltzman coefficient, respectively. The molecular shape of sulfides and aliphatic nitriles is not spheric, but as a first approximation, all molecules were treated as spheric molecules. The values of r for each system calculated as the sum of the radius of sphere for pair molecules are listed in Table 5. All dipole moments of aliphatic nitriles have not been reported. The dipole of aliphatic nitriles were calculated by HyperChem[22] after geometry optimization of molecular shapes of these aliphatic nitriles and are listed in Table 5. The geometry optimization was carried out by calculations using the AM1 method. The calculated value and observed value of dipole moment of MMTSO and DMSO showed closed agreement. Linear relationships were obtained as shown in Figure 4 between the excess partial molar enthalpies at infinite dilution of the mixtures of aliphatic nitriles and dipolar interaction energy terms of $\mu_1^2\mu_2^2(r_1 + r_2)^{-6}$. 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 nitriles. As shown in Figure 4, these behaviors of excess partial molar enthalpies were different between small nitriles and large nitriles. The boundary numbers of methylene for excess partial molar enthalpies of nitriles + sulfides were butyl groups. The coefficients of eq 7 for each field and the standard deviations are listed in Table 6

$$H_i^{E,\infty} = a_{dd} + b_{dd}\frac{\mu_1^2\mu_2^2}{(r^1 + r^2)^6} \qquad (7)$$

As shown in Table 6, coefficients b_{dd} of nitriles + DMSO in eq 7 were larger than those of nitriles + MMTSO. The 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 coefficients b_{dd} in eq 4 for the mixtures including DMSO were smaller than those of MMTSO. DMSO molecules (dipole moment = 13.4×10^{-30} C·m)[23] have larger dipolar stabilization than MMTSO molecules (10.7×10^{-30} C·m)[20] in the pure liquid state; the DMSO mixtures may absorb larger heat than the MMTSO mixtures, because of the insertion of weak polar molecules of the nitriles.

It was explained that the major effect on the excess enthalpies of solvent + MMTSO or DMSO might arise from the hindering of stable dipolar−dipolar contacts by the less polar components. However, the mixtures of aliphatic nitriles + MMTSO or DMSO have not only same effect as nonpolar solvent from the aliphatic part reported previously[6] but also additional, relatively large energetic effect from volume change on mixing.[24]

Literature Cited

(1) Kimura, T.; Takagi, S. Thermodynamics of Liquid Mixtures Containing Methyl Methylthiomethyl Sulfoxide. I. Excess Volumes of (Water +, Benzene +, Dimethyl Sulfoxide + Methyl Methylthiomethyl Sulfoxide) and (Water +, Benzene + Dimethyl Sulfoxide) at 298.15 and 318.15 K. *J. Chem. Thermodyn.* **1986**, *18*, 447−454.

(2) Kimura, T.; Takagi, S. Thermodynamics of Liquid Mixtures Containing Methyl Methylthiomethyl Sulfoxide. II Excess Enthalpies of (Water +, Benzene +, Dimethyl Sulfoxide + Methyl Methylthiomethyl Sulfoxide) and (Water +, Benzene + Dimethyl Sulfoxide) at 298.15 and 318.15 K. *Netsu Sokutei* **1986**, *13*, 2−8.

(3) Kimura, T.; Chanoki, T.; Mizuno, H.; Takagi, S. *Nippon Kagaku Kaishi* **1986**, 509−513.
(4) Kimura, T.; Takagi, S. Thermodynamics of Liquid Mixtures Containing Methyl Methyl Thiomethyl Sulfoxide. V. Excess Enthalpies of (Deuteriochloroform + Methyl Methylthiomethyl Sulfoxide), (Deuteriochloroform + Dimethyl Sulfoxide) and (Deuteriochloroform + Chloroform) at 298.15 K. *Thermochim. Acta* **1987**, *123*, 293−299.
(5) Kimura, T.; Morikuni, T.; Chanoki, T.; Takagi, S. Thermodynamics of Liquid Mixtures Containing Methlyl Methylthiomethyl Sulfoxide. VI Excess Enthalpies of (Methyl Methylthiomethyl Sulfoxide + Methanol, + Ethanol, + 1-Propanol) and (Dimethyl Sulfoxide + Methanol, + Ethanol, + 1-Propanol) at 298.15 K. *Netsu Soktei* **1990**, *17*, 67−72.
(6) Kimura, T.; Tsuji, T.; Usui, Y.; Takagi, S. Thermodynamics of Liquid Mixtures Containing Methyl Methyl Thiomethyl 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. *Thermochim. Acta* **1990**, *163*, 183−190.
(7) Kimura, T.; Tahara, T.; Takagi, S. Excess Enthalpies of (Methyl Methylthiomethyl Sulfoxide + Cycloethers) and (Dimethyl Sulfoxide + Cycloethers) at 298.15 K. *J. Therm. Anal.* **1992**, *38*, 1911−1920.
(8) Kimura, T.; Takagi, S. Excess Enthalpies of Diethyl Ether, Ethylpropyl Ether, Di-Propyl Ether + Methyl Methylthiomethy Sulfoxide or + Dimethy Sulfoxide at 298.15 K. *Thermochim. Acta* **1995**, *253*, 59−67.
(9) Kimura, T.; Tsuda, T.; Takagi, S. Excess Enthalpies of Chorobenzene, Chlorotoluene, Fluorobenzene, Bromobenzene, Fluorotoluene + Methyl Methylsulfoxide or + Dimethyl Sulfoxide at 298.15 K. *Thermochim. Acta* **1995**, *267*, 333−342.
(10) Kimura, T.; Takagi, S. Excess Enthalpies of Binary Mixtures with Oxepane, Oxetane, 3,4-Dihydro-2H-pyran, and Furan + Methyl Methyl Thiomethyl Sulfoxide and Dimethyl Sulfoxide at 298.15 K. *Netsu Sokutei* **1996**, *23*, 53−59.
(11) Kimura, T.; Suzuki, K.; Takagi, S. Excess Enthalpies of *o*- and *m*- Isomers of Difluorobenzene, Dichorobenzene, Dibromobenzene, + Methyl Methylthiomethy Sulfoxide or + Dimethyl Sulfoxide at 298.15 K. *Fluid Phase Equilib.* **1997**, *136*, 269−278.
(12) Kimura, T.; Sugihara, Y.; Takagi, S. Excess Volumes of Halogenized Aromatics + Methyl Methylthiomethyl Sulfoxide, + Dimethyl Sulfoxide at 298.15 K. *Fluid Phase Equilib.* **1997**, *136*, 323−331.
(13) Kimura, T.; Suzuki, K.; Takagi, S. Excess Enthalpies of Alkylbenzene + Methyl Methylthiomethy Sulfoxide or + Dimethyl Sulfoxide at 298.15 K. *Thermochim. Acta* **1999**, *328*, 55−64.
(14) Kimura, T.; Matsushita, T.; Kamiyama, T. Excess Enthalpies of Alkane-1-amines {$C_nH_{2n+1}NH_2$, n = 3 to n = 8} + Methyl Methlthiomethyl Sufoxide, + Dimethyl Sufoxide at 298.15 K *Thermochim. Acta* **2003**, *405*, 129−139.
(15) Kimura, T.; Matsushita, T.; Suzuki, K.; Takagi, S. Excess Enthalpies of Some Nitriles + Methyl Methylthiomethyl Sulfoxide or + Dimethyl Sulfoxide at 298.15 K. *Netsu Skukutei* **2004**, *31*, 61−68.
(16) Kimura, T.; Matsushita, T.; Kamiyama, T. Enthalpies of Solution of Aliphatic Compounds in Dimethyl Sulfoxide. *Thermochim. Acta* **2004**, *416*, 129−134.
(17) Takagi, S.; Kimura, T.; Maeda, M. Some Problems in Solution Calorimetry, Experimental Experiences by Authors, and Enthalpy-Entropy Compensation in Cyclodextrin + Alcohol Inclusion-Complex Formation in Aqueous Solutions. *Thermochim. Acta* **1985**, *88*, 247−254.
(18) Kimura, T.; Takagi, S. Excess Enthalpies of Mixing at 298.15 K of the Systems: Benzene + Carbon Tetrachloride and Chlorobenzene + Toluene. Reliability Test of a Calorimeter with Relatively Small Amounts of Samples. *J. Fac. Sci. Technol. Kinki Univ.* **1983**, *18*, 49−55.
(19) Kimura, T.; Matsushita, T.; Mizuno, S.; Momota, M.; Toshiyasu, Y.; Kamiyama, T.; Takagi, S. *J. Therm. Anal. Calorim.* **2001**, *64*, 231−241.
(20) Kimura, T.; Matsushita, T.; Momoki, M.; Mizuno, H.; Kanbayashi, N.; Kamiyama, T.; Fujisawa, M.; Takagi, S.; Toshiyasu, Y. Excess enthalpies of {Methyl Methylthiomethyl Sulfoxide + ($C_nH_{2n+1}OH$, n=4∼12)} and {Dimethyl Sulfoxide + ($C_nH_{2n+1}OH$, n=4∼12)} at 298.15 K. *Thermochim. Acta*, in press.
(21) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 3rd ed.; John Wiley & Sons: New York, 1986.
(22) HyperChem version 7, HYPERCUBE, Inc.
(23) Pekary, A. E. Dipole Moment and Far-Infrared Studies on the Dimethyl Sulfoxide-Iodine Complex. *J. Phys. Chem.* **1974**, *78*, 1744−1746.
(24) Kimura, T.; Matsushita, T.; Sunada, N.; Miura, S.; Takagi, S. To be published.

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