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Excess enthalpies of $\{CH_3(CH_2)_nOH,\ n = 3–12\}$ + methyl methylthiomethyl sulfoxide or dimethyl sulfoxide at 298.15 K

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Abstract

Excess enthalpies of nine mixtures between methyl methylthiomethyl sulfoxide (MMTSO) or dimethyl sulfoxide (DMSO) and each of aliphatic alcohols $\{CH_3(CH_2)_nOH,\ n = 3–11\}$ have been determined at 298.15 K. All the systems show the positive enthalpies over the whole range of mole fraction. Excess enthalpies of MMTSO + alcohols are larger than that of DMSO + alcohols and increased with increasing the number of methylene groups of alcohols. The excess partial molar enthalpies at infinite dilution of butane-1-ol showed the boundary between the two linear relationships obtained between those of MMTSO or DMSO and dipole–dipole interaction of aliphatic alcohols$\{CH_3(CH_2)_nOH,\ n = 0–11\}$-sulfoxides.

Keywords: Excess enthalpy; MMTSO; DMSO; Aliphatic alcohols; Excess partial molar enthalpy

1. Introduction

In our previous papers, excess thermodynamic functions for the binary mixtures of methyl methylthiomethyl sulfoxide (MMTSO) and water, benzene, dimethyl sulfoxide (DMSO) [1,2], carbon tetrachloride, chloroform, dichloromethane [3], deuterochloroform [4], methanol, ethanol, 1-propanol [5], six methylbenzenes $\{C_6H_{6-n}(CH_3)_n,\ n = 1–3\}$ [6], five cycloethers [7], three aliphatic ethers [8], five monohalogenated aromatic compounds (benzene and toluene) [9], three aliphatic ethers [10], six *o*- and *m*-dihalogenated benzenes [11], aliphatic benzene [12], aliphatic amine [13], some nitriles $\{[CH_3(CH_2)_nCN,\ n = 0–12]$, benzonitrile$\}$ [14,15] and those of DMSO were reported.

To find a size effect of non-polar group in alcohols on the thermodynamic properties of mixtures, excess enthalpies of the mixtures between MMTSO and nine aliphatic alcohols from butane-1-ol to dodecane-1-ol were determined over the whole range of mole fractions. Results are compared with those of previous aliphatic compounds to clarify the correlation between thermodynamic properties of the mixtures and molecular structures of their components. Those of aliphatic alcohols + 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]. Butane-1-ol to dodecane-1-ol (Tokyo Kasei Chemical, GR) were fractionally distilled through 1 m column over freshly activated molecular sieves 3 or 4 A 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

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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 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 ± 0.001 K over the whole range of mole fraction. The details of calorimetric procedures and reproducibility test of this calorimeter system were described elsewhere [2,4,10,16].

Measurements of relative dielectric constants were carried out at 298.2 ± 0.02 K by the same apparatus and procedures as in previous work [17].

3. Results and discussion

The dipole moment of MMTSO was determined with the use of the density of MMTSO of 1.21618 g cm^{-3} at 298.15 K [1]. The experimental results of dipole moment obtained are summarized in Table 1. The excess enthalpies are summarized in Table 2 and plotted in Figs. 1 and 2. They were fitted with Eq. (1) by the method of least squares:

Table 1
Dipole moment μ of MMTSO in C m

10.7×10^{-30}
10.5×10^{-30}
10.5×10^{-30}
10.8×10^{-30}
10.8×10^{-30}

Average 10.7×10^{-30} C m, $s_f = 0.15 \times 10^{-30}$ C m.

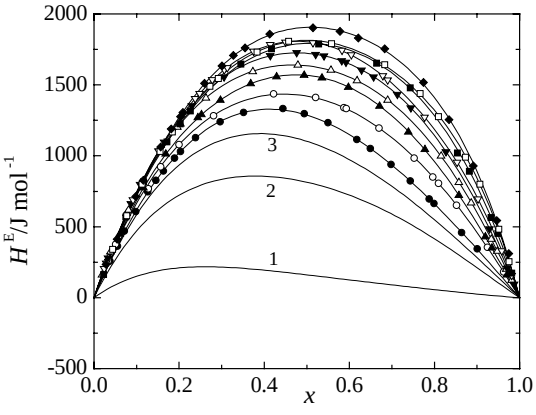

Fig. 1. Excess enthalpies of mixing at 298.15 K: $(1-x)C_nH_{2n+1}OH + x$MMTSO: 1, $n = 1$; 2, $n = 2$; 3, $n = 3$; (●) $n = 4$; (○) $n = 5$; (▲) $n = 6$; (△) $n = 7$; (▼) $n = 8$; (▽) $n = 9$; (■) $n = 10$; (□) $n = 11$; (◆) $n = 12$. Smoothed curves were calculated from Eq. (1) with coefficients in Table 3. The curves 1–3 were cited from Ref. [5].

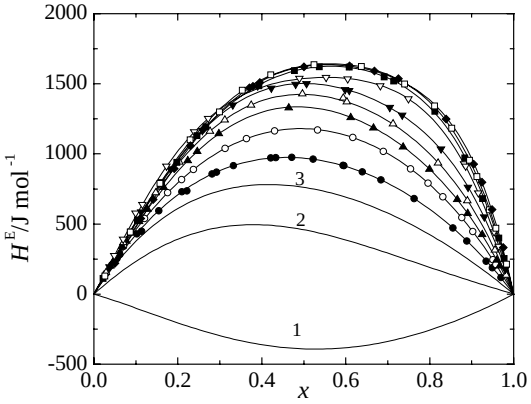

Fig. 2. Excess enthalpies of mixing at 298.15 K: $(1-x)C_nH_{2n+1}OH + x$DMSO: 1, $n = 1$; 2, $n = 2$; 3, $n = 3$; (●) $n = 4$; (○) $n = 5$; (▲) $n = 6$; (△) $n = 7$; (▼) $n = 8$; (▽) $n = 9$; (■) $n = 10$; (□) $n = 11$; (◆) $n = 12$. Smoothed curves were calculated from Eq. (1) with coefficients in Table 3. The curves 1–3 were cited from reference 5.

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

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

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

were given in Table 3.

All the excess enthalpies observed here for alkane-1-ol + MMTSO were positive over the whole range of mole fractions at the temperature. Excess enthalpies of methanol to propane-1-ol [5] were also potted in Fig. 1 for the sake of comparison. The excess enthalpies of alcohols + MMSTO were increased with increasing size of aliphatic groups of aliphatic alcohols as the mixtures of aliphatic amines + MMTSO [13] and aliphatic nitriles + MMTSO [14,15]. 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 interaction between sulfoxides and alcohols.

Excess enthalpies of aliphatic alcohols compounds + DMSO observed were positive over the whole range of mole fractions at this temperature and showed a similar behavior as those of aliphatic alcohols + MMTSO as shown in Fig. 2 except the mixtures of methanol + DMSO. The negative excess enthalpies were obtained only for the system of methanol + DMSO over the whole range of mole fraction as shown in Fig. 2.

Excess enthalpies of aliphatic alcohols $\{CH_3(CH_2)_nOH$, $n = 0$–$6\}$ + DMSO were reported by Chao et al. [18]. Those values were 7–24% smaller than this work and the difference between their excess enthalpy values and those of the this work were increased with increasing the size of aliphatic groups of alcohols. Their results were measured by Picker flow type calorimeter. In generally flow type calorimetry

Table 2
Excess enthalpies of (1−x) aliphatic alcohols + xMMTSO or +xDMSO 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})
(1 − x)C_4H_9OH + xMMTSO							
0.03718	258.52	0.16333	893.45	0.44378	1332.6	0.74301	824.07
0.05491	364.70	0.18926	984.49	0.49401	1296.5	0.78726	695.55
0.07161	470.00	0.20300	1030.0	0.54952	1233.1	0.79880	664.82
0.09796	606.40	0.23839	1128.7	0.61728	1115.7	0.86370	459.10
0.12660	747.57	0.29639	1240.2	0.64921	1052.0	0.90023	343.90
0.14521	827.05	0.35164	1306.6	0.69795	939.46		
(1 − x)$C_5H_{11}OH$ + xMMTSO							
0.03397	260.00	0.28082	1283.4	0.59276	1333.9	0.80975	805.33
0.05112	375.66	0.42209	1436.1	0.66977	1196.1	0.85161	652.13
0.12767	767.78	0.52117	1412.4	0.75262	984.75	0.92446	354.70
0.15698	923.41	0.58730	1340.2	0.79592	850.37	0.96226	182.33
0.19997	1078.7						
(1 − x)$C_6H_{13}OH$ + xMMTSO							
0.06044	448.19	0.29696	1392.5	0.59801	1484.0	0.85737	722.48
0.11644	774.81	0.36847	1508.0	0.67145	1350.8	0.91959	429.10
0.16858	1012.6	0.42883	1557.1	0.73913	1168.6	0.93506	350.94
0.24447	1269.5	0.49423	1568.4	0.77763	1044.8	0.97019	161.51
0.25230	1290.0	0.53531	1549.5				
(1 − x)$C_7H_{15}OH$ + xMMTSO							
0.01887	160.16	0.19637	1202.0	0.55685	1604.4	0.88655	667.86
0.03387	281.56	0.20309	1226.0	0.61851	1530.4	0.93374	412.02
0.03884	323.76	0.26319	1407.5	0.69051	1392.6	0.94801	328.02
0.07695	594.88	0.37342	1592.6	0.81558	998.43	0.96883	200.64
0.08124	617.97	0.47915	1640.0	0.85748	813.13	0.98191	122.38
(1 − x)$C_8H_{17}OH$ + xMMTSO							
0.03326	278.98	0.30525	1555.9	0.58254	1670.2	0.74480	1337.5
0.08696	662.59	0.41395	1705.9	0.59199	1658.6	0.82720	1028.9
0.1088	798.23	0.47637	1725.9	0.62871	1603.3	0.92953	485.26
0.16526	1095.7	0.52047	1713.8	0.65732	1555.0	0.97077	208.04
0.23013	1352.5	0.54027	1702.9	0.71263	1431.9	0.98746	95.81
(1 − x)$C_9H_{19}OH$ + xMMTSO							
0.02419	204.34	0.27783	1535.8	0.51439	1796.9	0.77674	1271.9
0.02893	243.92	0.30608	1606.5	0.58279	1743.1	0.85327	955.04
0.09179	690.58	0.31328	1621.3	0.60498	1712.1	0.90226	695.13
0.15206	1034.6	0.37456	1737.5	0.67879	1564.4	0.95843	329.99
0.23783	1402.9	0.41434	1784.0	0.69053	1533.5	0.98199	156.89
0.24843	1438.9	0.45019	1800.1				
(1 − x)$C_{10}H_{21}OH$ + xMMTSO							
0.02243	179.74	0.20227	1224.2	0.52771	1787.5	0.88194	889.88
0.07502	564.69	0.22652	1315.7	0.66387	1652.8	0.93289	562.50
0.11677	817.71	0.34476	1645.8	0.74339	1478.8	0.94890	451.64
0.17164	1098.5	0.41731	1754.9	0.85894	1019.1	0.98158	173.12
(1 − x)$C_{11}H_{23}OH$ + xMMTSO							
0.04387	343.65	0.27263	1490.7	0.55819	1791.2	0.87298	991.07
0.07668	578.31	0.29183	1545.6	0.68330	1642.8	0.90680	800.60
0.11263	800.60	0.38287	1732.1	0.76645	1438.7	0.95098	479.20
0.15506	1030.3	0.45736	1806.6	0.80967	1278.3	0.97531	252.98
0.18429	1169.1						
(1 − x)$C_{12}H_{25}OH$ + xMMTSO							
0.02802	227.29	0.20320	1279.0	0.41299	1858.3	0.77398	1506.7
0.05441	411.46	0.20918	1306.3	0.51473	1903.2	0.83404	1257.2
0.09822	712.87	0.25946	1511.0	0.57794	1877.1	0.89157	939.77
0.11545	827.05	0.30029	1633.3	0.62069	1830.2	0.9466	540.06
0.1565	1062.2	0.32749	1708.3	0.68287	1750.2	0.97494	271.55
0.18154	1189.6	0.35470	1760.4				
(1 − x)C_4H_9OH + xDMSO							
0.05488	252.93	0.22150	735.42	0.47134	976.40	0.76286	680.48

Table 2 (*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})
0.06224	283.75	0.28169	857.40	0.52192	963.42	0.8551	471.55
0.10224	429.70	0.29215	870.38	0.59321	917.40	0.88823	378.43
0.1139	449.16	0.33229	916.71	0.59545	916.67	0.93467	234.86
0.15464	594.50	0.42162	972.08	0.63932	872.49	0.94916	188.85
0.20991	730.42	0.43345	972.50	0.68412	815.28	0.96966	117.14
$(1-x)C_5H_{11}OH + x$DMSO							
0.02908	147.34	0.20858	817.26	0.53275	1170.2	0.83124	693.96
0.04232	207.11	0.23723	889.15	0.61694	1117.1	0.87631	545.20
0.07078	340.50	0.31262	1039.5	0.68942	1017.7	0.90274	446.08
0.12049	540.32	0.36375	1108.8	0.75408	893.52	0.95061	244.54
0.17603	723.63	0.43073	1163.2	0.79596	792.22	0.95775	211.92
$(1-x)C_6H_{13}OH + x$DMSO							
0.03972	199.84	0.1276	604.19	0.46432	1329.9	0.86578	675.90
0.04521	227.85	0.16647	760.95	0.61198	1258.1	0.89095	575.55
0.06802	339.81	0.22381	951.45	0.66647	1185.8	0.92499	424.02
0.07733	378.97	0.24617	1017.9	0.73687	1049.6	0.95992	242.42
0.10801	517.28	0.29784	1145.6	0.79967	889.81	0.96681	200.40
$(1-x)C_7H_{15}OH + x$DMSO							
0.029	153.88	0.27644	1161.6	0.59443	1398.2	0.88971	666.92
0.07062	367.59	0.31187	1242.2	0.60239	1370.8	0.95525	316.01
0.14722	722.64	0.37464	1348.3	0.71300	1213.6	0.98223	134.11
0.20389	941.17	0.49655	1427.4	0.81976	935.56		
$(1-x)C_8H_{17}OH + x$DMSO							
0.03712	193.60	0.33122	1347.8	0.59817	1458.7	0.82684	1034.7
0.11324	585.56	0.42282	1469.5	0.60856	1451.4	0.89167	762.22
0.18221	892.44	0.48032	1496.4	0.70526	1330.8	0.93002	550.28
0.25835	1165.4	0.50671	1499.7	0.73458	1276.6	0.98013	178.39
$(1-x)C_9H_{19}OH + x$DMSO							
0.04857	275.36	0.23912	1156.6	0.60512	1535.1	0.88550	910.91
0.06967	390.56	0.27245	1253.3	0.68244	1485.0	0.91621	720.72
0.09957	576.80	0.39039	1482.7	0.74965	1391.9	0.95308	443.80
0.11601	638.20	0.48983	1538.1	0.88207	927.98	0.96495	339.93
0.17302	912.56	0.55320	1544.7				
$(1-x)C_{10}H_{21}OH + x$DMSO							
0.02200	112.21	0.24583	1130.2	0.60843	1619.3	0.88344	978.43
0.08668	442.75	0.26693	1193.1	0.69143	1549.1	0.92853	682.71
0.10380	529.43	0.39285	1485.5	0.71439	1519.2	0.96446	390.24
0.16090	794.81	0.47763	1594.0	0.81201	1300.3	0.97715	253.17
0.19756	939.01	0.53684	1621.0				
$(1-x)C_{11}H_{23}OH + x$DMSO							
0.02632	128.74	0.35359	1453.5	0.74033	1497.5	0.91105	841.86
0.08708	441.90	0.42118	1564.8	0.81173	1340.8	0.94248	600.71
0.15758	790.17	0.52429	1636.3	0.85246	1182.1	0.95793	469.09
0.22922	1092.4	0.63753	1622.5	0.89485	954.43	0.98320	202.71
0.29899	1312.1						
$(1-x)C_{12}H_{25}OH + x$DMSO							
0.04995	228.75	0.26125	1175.5	0.60914	1628.2	0.90485	926.45
0.11136	539.97	0.37031	1469.8	0.66832	1591.4	0.92475	796.82
0.14120	674.31	0.37902	1482.0	0.72533	1536.6	0.94830	603.45
0.19100	895.83	0.39485	1509.8	0.83890	1258.1	0.97538	322.13
0.22987	1058.5	0.50068	1621.2				

gave small enthalpy change when the fluids used were viscous.

Excess enthalpies of aliphatic alcohols {$CH_3(CH_2)_nOH$, $n = 0-12$} + MMTSO were larger than those of aliphatic alcohols + DMSO, respectively. This size effect of aliphatic groups on excess enthalpies was similar behavior compared with all other mixtures containing aliphatic benzene [12] and aliphatic amines [13], except the mixtures of aliphatic nitriles + MMTSO [14,15].

Table 3
Best-fit values for the coefficients A_i of Eq. (1) with the standard deviations of the fit s_f

System	A_1	A_2	A_3	A_4	A_5	s_f (J mol^{-1})
$(1-x)C_4H_9OH + x$MMTSO	5149.3	1845.5	295.7	105.3		2.4
$(1-x)C_5H_{11}OH + x$MMTSO	5684.9	1048.9	876.6	581.7		2.8
$(1-x)C_6H_{13}OH + x$MMTSO	6270.5	561.0	711.9	883.2		1.8
$(1-x)C_7H_{15}OH + x$MMTSO	6540.3	643.2	1791.6	483.8	−623.7	2.1
$(1-x)C_8H_{17}OH + x$MMTSO	6889.4	463.1	1767.2	186.5	−509.6	2.0
$(1-x)C_9H_{19}OH + x$MMTSO	7219.4	559.2	963.4	−517.7	545.0	2.6
$(1-x)C_{10}H_{21}OH+x$MMTSO	7172.4	−150.3	1658.4	−500.2	303.3	4.6
$(1-x)C_{11}H_{23}OH + x$MMTSO	7255.5	−14.3	1734.4	−1231.0	816.7	4.9
$(1-x)C_{12}H_{25}OH + x$MMTSO	7619.8	−183.6	2054.0	−1478.3	119.1	5.8
$(1-x)CH_3OH+x$MMTSO[a]	643.7	703.0	527.7	265.0		1.0
$(1-x)C_2H_5OH + x$MMTSO[a]	3256.8	1346.6	826.8	700.8		1.4
$(1-x)C_3H_7OH + x$MMTSO[a]	4411.8	1888.8	636.4	330.0		2.1
$(1-x)C_4H_9OH + x$DMSO	3877.6	922.9	516.9	135.2		1.9
$(1-x)C_5H_{11}OH + x$DMSO	4719.7	121.7	566.1	−160.9		1.8
$(1-x)C_6H_{13}OH + x$DMSO	5337.0	278.1	509.5	−983.6		2.3
$(1-x)C_7H_{15}OH + x$DMSO	5696.4	122.7	914.1	−1385.5		2.0
$(1-x)C_8H_{17}OH + x$DMSO	6008.4	−23.3	1361.8	−2159.9		2.4
$(1-x)C_9H_{19}OH + x$DMSO	6151.7	−580.8	3273.5	−1979.8	−1380.7	2.3
$(1-x)C_{10}H_{21}OH + x$DMSO	6424.4	−1134.1	1951.7	−2295.3	168.5	4.9
$(1-x)C_{11}H_{23}OH + x$DMSO	6512.4	−979.3	2290.7	−2964.8	−88.7	5.3
$(1-x)C_{12}H_{25}OH + x$DMSO	6490.2	−985.2	1799.9	−3754.8	947.6	5.7
$(1-x)CH_3OH + x$DMSO[a]	−1562.4	220.6	327.1	127.0		0.9
$(1-x)C_2H_5OH + x$DMSO[a]	1835.8	1135.7	−43.2	−246.8		0.9
$(1-x)C_3H_7OH + x$DMSO[a]	3047.0	922.9	516.9	135.2		1.3

[a] Cited from reference [5].

Table 4
Excess partial molar enthalpies at infinite dilution at 298.15 K and $\mu_1^2\mu_2^2(r_1+r_2)^{-6}$ of aliphatic alcohols + MMTSO or +DMSO

System	$H_1^{E,\infty}$ (kJ mol^{-1})	$H_2^{E,\infty}$ (kJ mol^{-1})	$10^{62}\mu_2^1\mu_2^2/(r_1+r_2)^6$ (C^4 m^{-2})
$(1-x)C_4H_9OH + x$MMTSO	3.49	7.40	0.34
$(1-x)C_5H_{11}OH + x$MMTSO	4.93	8.19	0.29
$(1-x)C_6H_{13}OH + x$MMTSO	5.54	8.43	0.26
$(1-x)C_7H_{15}OH + x$MMTSO	6.58	8.84	0.24
$(1-x)C_8H_{17}OH + x$MMTSO	7.50	8.80	0.21
$(1-x)C_9H_{19}OH + x$MMTSO	8.69	8.77	0.19
$(1-x)C_{10}H_{21}OH + x$MMTSO	9.79	8.49	0.17
$(1-x)C_{11}H_{23}OH + x$MMTSO	11.1	8.56	0.16
$(1-x)C_{12}H_{25}OH + x$MMTSO	11.5	8.13	0.14
$(1-x)CH_3OH + x$MMTSO[a]	0.20	2.14	0.69
$(1-x)C_2H_5OH + x$MMTSO[a]	2.04	6.13	0.50
$(1-x)C_3H_7OH + x$MMTSO[a]	2.83	7.27	0.40
$(1-x)C_4H_9OH + x$DMSO	3.34	5.45	1.19
$(1-x)C_5H_{11}OH + x$DMSO	5.33	5.25	1.02
$(1-x)C_6H_{13}OH + x$DMSO	6.55	5.14	0.91
$(1-x)C_7H_{15}OH + x$DMSO	7.87	5.35	0.83
$(1-x)C_8H_{17}OH + x$DMSO	9.55	5.19	0.73
$(1-x)C_9H_{19}OH + x$DMSO	10.6	5.48	0.66
$(1-x)C_{10}H_{21}OH + x$DMSO	12.0	5.12	0.59
$(1-x)C_{11}H_{23}OH + x$DMSO	12.7	4.83	0.54
$(1-x)C_{12}H_{25}OH + x$DMSO	14.0	4.43	0.49
$(1-x)CH_3OH + x$DMSO[a]	−1.58	−0.89	2.53
$(1-x)C_2H_5OH + x$DMSO[a]	0.90	2.68	1.79
$(1-x)C_3H_7OH + x$DMSO[a]	2.51	4.62	1.44

[a] Cited from reference [5].

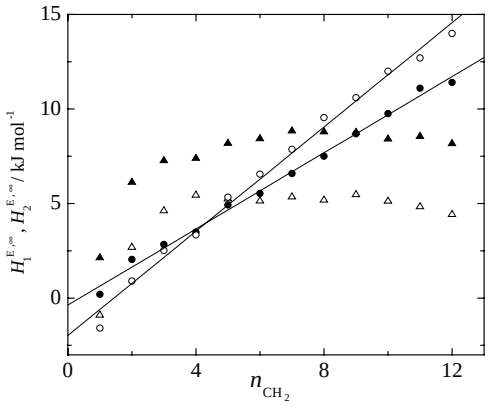

Fig. 3. Correlation between excess partial molar enthalpies at infinite dilution and number of methylene groups of aliphatic alcohols: (●) $H_1^{E,\infty}$(MMTSOMM) (kJ mol^{-1}); (▲) $H_2^{E,\infty}$(MMTSO) (kJ mol^{-1}); (○) $H_1^{E,\infty}$(DMSO) (kJ mol^{-1}); (△) $H_2^{E,\infty}$(DMSO) (kJ mol^{-1}).

For the sake of an elementary consideration of pair wise interaction, excess partial molar enthalpies at infinite dilutions were determined from Eq. (1) with the coefficients in Table 3, and summarized in Table 4. Correlation between excess partial molar enthalpies at infinite dilution and the number of methylene groups were plotted in Fig. 3. The excess partial molar enthalpies at infinite dilution of aliphatic alcohol $H_1^{E,\infty}$ of aliphatic alcohols + MMTSO and aliphatic alcohols + DMSO increased with increasing size of the aliphatic groups. Correlation between excess partial molar enthalpies at infinite dilution of aliphatic alcohols and the number of methylene groups were fitted following equations:

$$H_1^{E}(\text{MMTSO})\ (\text{kJ mol}^{-1}) - 0.37 + 1.01n_c,\quad s_f = 0.28\ \text{kJ mol}^{-1} \tag{3}$$

$$H_1^{E}(\text{DMSO})\ (\text{kJ mol}^{-1}) - 1.98 + 1.38n_c,\quad s_f = 0.48\ \text{kJ mol}^{-1} \tag{4}$$

The hydrophobicity of aliphatic alcohols may depend on the number of methylene groups in the aliphatic alcohols. The slopes of Eqs. (3) and (4) determined were positive and showed unfavorable interaction between sulfoxides and aliphatic groups of methylene. The size of methylene group might induce the enhancement of unfavorable interaction between sulfoxides and aliphatic alcohols. The slops of excess partial molar enthalpies of the mixtures of DMSO were larger than those of the mixtures of MMTSO.

The excess partial molar enthalpies at infinite dilution $H_2^{E,\infty}$ of MMTSO or DMSO of aliphatic alcohols+MMTSO and aliphatic alcohol+DMSO were shown very different behavior compared with $H_1^{E,\infty}$. Especially, $H_2^{E,\infty}$ of aliphatic alcohols which have large aliphatic groups more than butane showed very different behavior comparing with the system containing aliphatic amines [13] and aliphatic nitriles [15].

The excess partial molar enthalpies at infinite dilution of alcohol $H_1^{E,\infty}$ of the aliphatic alcohols + MMTSO were smaller than those of MMTSO $H_2^{E,\infty}$ for the mixtures containing alcohols {$CH_3(CH_2)_nOH$, n = 0–8} but vice versa for the mixtures containing alcohols {$CH_3(CH_2)_nOH$, n = 9–12}. The excess partial molar enthalpies at infinite dilution of aliphatic alcohols + DMSO were almost same behaviors as those of aliphatic alcohols + MMTSO. When aliphatic group was smaller than pentane, $H_1^{E,\infty}$ of the aliphatic alcohols + DMSO were smaller than those of DMSO $H_2^{E,\infty}$ but vice versa for the mixtures containing alcohols {$CH_3(CH_2)_nOH$, n = 5–12}. The similar results of the mixtures of alcohols {$CH_3(CH_2)_nOH$, n = 0–8}+MMTSO were obtained for the mixture of water [2], chloromethanes [3,4], although methylbenzenes [6], cycloethers [7], and aliphatic amines {$C_nH_{2n+1}NH_2$, n = 3–8} [13], and nitriles {$CH_3(CH_2)_nCN$, n = 6–12} + MMTSO were different. The excess partial molar enthalpies of aliphatic alcohols at infinite dilution $H_1^{E,\infty}$ for aliphatic alcohols + DMSO were less unstable than those for the aliphatic alcohols + MMTSO for all mixture of aliphatic alcohols measured.

The amphiphiles of aliphatic alcohols have two opposite interaction between sulfoxides. There might be not small dipole–dipole interaction effects on the limiting excess partial molar enthalpies of the mixtures between alcohols and sulfoxides. The dipole–dipole interaction energy of pair molecules [19] were shown as

$$u_{12} = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{r^6 kT} \tag{5}$$

where μ, r and k are dipole moment, distance between molecules and Boltzmann coefficient, respectively. The molecular shape of sulfoxides and aliphatic alcohols are not sphere, but as a first approximation, all molecules were treated as sphere molecules. The values of r for each system calculated as sum of radius of sphere for pair molecules are listed in Table 5. All dipole moment of aliphatic alcohols have not been reported. The dipoles of aliphatic alcohols were calculated by HyperChem [20] after geometry optimization of molecular shapes of these aliphatic alcohols, and were listed in Table 5. The geometry optimizations 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. Correlations between the excess partial molar enthalpies at infinite dilution of $H_1^{E,\infty}$ or $H_2^{E,\infty}$ and dipolar interaction energy terms of $\mu_1^2\mu_2^2(r_1 + r_2)^{-6}$ were shown in Fig. 4. Linear relationships were obtained as shown in Fig. 4. Excess partial molar enthalpies at infinite dilution of the mixtures containing MMTSO or DMSO decreased with increasing the dipolar interaction energy terms between sulfoxides and alcohols except $H_1^{E,\infty}$ of {$CH_3(CH_2)_nOH$, n = 5–12} + DMSO. As shown in Fig. 4, these behaviors of excess partial molar enthalpies were different between small alcohols and large alcohols. The boundary numbers of methylene for excess partial molar enthalpies of alcohols + sulfoxides were butyl

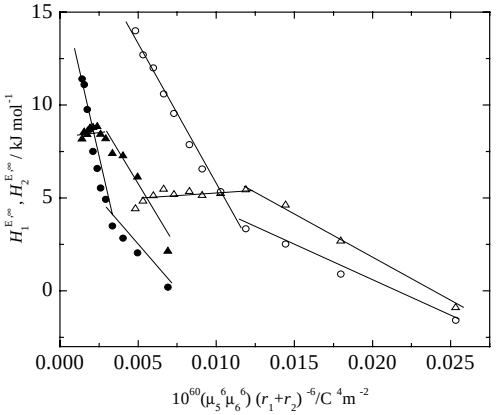

Fig. 4. Correlation between excess partial molar enthalpies at infinite dilution and $\mu_1^2\mu_2^2(r_1+r_2)^{-6}$ of aliphatic alcohols+MMTSO or +DMSO: (●) $H_1^{E,\infty}$(MMTSO); (▲) $H_2^{E,\infty}$(MMTSO); (○) $H_1^{E,\infty}$(DMSO); (△) $H_2^{E,\infty}$(DMSO).

group. It was almost same behaviors of the mixture of the aliphatic nitriles + the sulfoxides. The coefficients of Eq. (6) for each field and the standard deviations are listed in Table 6:

$$H_i^{E,\infty}\ (\mathrm{kJ\,mol^{-1}}) = a_{dd} + b_{dd}\frac{\mu_1^2\mu_2^2}{(r_1+r_2)^6} \quad (6)$$

As shown in Table 6, coefficients b_{dd} of alcohols + DMSO in Eq. (6) were larger than those of alcohols + MMTSO. DMSO molecule has not only the smallest volume and the largest dipole moment but also the most spherical molecule than MMTSO 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. (6) for the mixtures including DMSO were smaller than those of MMTSO. Because DMSO molecules (dipole moment: 13.4×10^{-30} C m) [21] have larger dipolar stabilization than MMTSO molecules (10.7×10^{-30} C m) in pure liquid state, the DMSO mixtures may absorb larger heat than the MMTSO mixtures, owing to the insertion of weak polar molecule of the alcohols. Those behaviors are almost same as nitriles + MMTSO or +DMSO.

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.

Table 5
Calculated physical properties of aliphatic alcohols and sulfoxides

System	$10^{30}\mu$ (C m)	$10V$ (nm^3)	r (nm)
CH_3OH	5.41	1.84	0.353
C_2H_5OH	5.17	2.42	0.386
C_3H_7OH	5.12	2.95	0.413
C_4H_9OH	5.07	3.50	0.437
$C_5H_{11}OH$	5.08	4.04	0.459
$C_6H_{13}OH$	5.04	4.46	0.474
$C_7H_{15}OH$	5.07	4.92	0.490
$C_8H_{17}OH$	5.03	5.45	0.507
$C_9H_{19}OH$	5.06	5.98	0.523
$C_{10}H_{21}OH$	5.03	6.52	0.539
$C_{11}H_{23}OH$	5.04	7.01	0.555
$C_{12}H_{25}OH$	5.04	7.52	0.571
MMTSO	8.17	4.00	0.457
DMSO	13.2	2.92	0.412
MMTSO	10.7[a]		
DMSO	13.4[b]		

μ, dipole moment; V, volume; r, radius.
[a] This work.
[b] Cited from reference [21].

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Table 6
Best fit for the coefficients of Eq. (6) ($H_1^{E,\infty} = a_{dd} + b_{dd}(\mu_1^2\mu_2^2)(r_1+r_2)^{-6}$)

System	nCH$_2$	a_{dd} (kJ mol^{-1})	$10^{60}b_{dd}$ (kJ mol^{-1} C^{-4} m^2)	s_f (kJ mol^{-1} C^{-1} m^{-2})
Aliphatic alcohol + MMTSO	1–4 ($H_1^{E,\infty}$)	6.58	−920	0.04
Aliphatic nitrile + MMTSO [14]	1–4 ($H_1^{E,\infty}$)	5.27	−214	0.15
Aliphatic alcohol + MMTSO	5–12 ($H_1^{E,\infty}$)	17.8	−4626	0.43
Aliphatic nitrile + MMTSO [15]	5–13 ($H_1^{E,\infty}$)	13.6	−942	0.33
Aliphatic alcohol + MMTSO	1–4 ($H_2^{E,\infty}$)	13.2	−1552	0.70
Aliphatic nitrile + MMTSO [14]	1–4 ($H_2^{E,\infty}$)	5.00	−130	0.02
Aliphatic alcohol + MMTSO	5–12 ($H_2^{E,\infty}$)	8.52	−2.7	0.28
Aliphatic nitrile + MMTSO [15]	5–13 ($H_2^{E,\infty}$)	7.62	−367	0.19
Aliphatic alcohol + DMSO	1–4 ($H_1^{E,\infty}$)	7.74	−370	0.16
Aliphatic nitrile + DMSO [14]	1–4 ($H_1^{E,\infty}$)	9.25	−136	0.15
Aliphatic alcohol + DMSO	5–12 ($H_1^{E,\infty}$)	21.43	−1608	0.29
Aliphatic nitrile + DMSO [15]	5–9 ($H_1^{E,\infty}$)	18.5	−367	0.29
Aliphatic nitrile + DMSO	10–13 ($H_1^{E,\infty}$)	12.4	−76.3	0.17
Aliphatic alcohol + DMSO	1–4 ($H_1^{E,\infty}$)	11.4	−482	0.20
Aliphatic nitrile + DMSO [14]	1–4 ($H_2^{E,\infty}$)	7.03	−97.0	0.18
Aliphatic alcohol + DMSO	5–12 ($H_2^{E,\infty}$)	4.34	105	0.28
Aliphatic nitrile + DMSO [15]	5–13 ($H_2^{E,\infty}$)	5.13	−55	0.18

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