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EXCESS ENTHALPIES OF CYCLOETHER + METHYL METHYLTHIOMETHYL SULFOXIDE OR DIMETHYL SULFOXIDE AT 298.15 K

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Excess enthalpies of ten binary mixtures of each of methyl methylthiomethyl sulfoxide (MMTSO) and dimethyl sulfoxide (DMSO) with one of the cycloethers (oxane, 1,3- and 1,4-dioxanes, oxolane and 1,3-dioxolane) have been determined at 298.15 K. All the mixtures show positive excess enthalpies over the whole composition range. Excess enthalpies of the cycloether + MMTSO or DMSO decrease with increasing number of oxygen atoms in the cycloether molecules, except for oxolane + MMTSO. Excess enthalpies of MMTSO + cycloethers are smaller than those of DMSO + cycloethers for the same cycloether except for the 1,3-dioxolane mixtures.

Keywords: binary mixtures, excess enthalpies

Introduction

In our previous papers [2–7], 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 (n=1 to 9) and six methylbenzenes ($C_6H_{6-n}(CH_3)_n$, n = 1 to 3) and those of DMSO were reported.

In order to find a correlation between the thermodynamic properties of the mixtures and molecular structures of their components, excess enthalpies of the mixtures of MMTSO with some cycloethers (1,3- and 1,4-dioxanes, oxane, oxolane and 1,3-dioxolane) were determined over the whole composition range.

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Experimental

Materials

Procedures of purification and the final purities of MMTSO (Nippon Soda Co.) and DMSO (Merck, uvasol) were the same as those described previously [2, 3]. Oxane (tetrahydropyran, Aldrich, anhydrous), 1.4-dioxane (Kishida, GR), 1,3-dioxane (Tokyo Kasei, GR), oxolane (tetrahydrofuran, Kishida, GR), and 1,3-dioxolane (Tokyo, Kasei, 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. GC 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 titration by a Moisture meter (Mitsubishi Chemical Ind., CA–02) gave the water content of each sample to be 0.01 mole per cent or less.

Apparatus and procedures

A twin-microcalorimeter of heat-conduction type (laboratory designation MC-AII) [3, 5, 8] was used for measurements of excess enthalpies at 298.15 K over the whole composition range. Pure liquids and the mixtures were loaded from weighed gas-tight syringes (Hamilton 1001TLL or 1002TLL) fitted with suitably bent stainless-steel needles (Hamilton HF730). A semi-microbalance (Mettler H20) was used before and after loading in a thermostated room. The details of calorimetric procedures and the reproducibility test of this calorimeter system were described elsewhere [5, 8].

Results and discussion

The experimental results of excess enthalpies obtained are summarized in Table 1 and plotted in Figs 1 and 2. They were fitted by Eq. (1) by the method of least squares

$$H^{\mathrm{E}} = (1-x)x\sum_{\mathrm{i=1}}^{\mathrm{k}} A_{\mathrm{i}}(1-2x)^{\mathrm{i}-1} \tag{1}$$

The coefficients A_{i} in Eq. (1) and standard deviations of the fits s_{f}:

$$s_{\mathrm{f}} = \left[\frac{\sum_{\mathrm{i=1}}^{\mathrm{n}} \left\{H_{\mathrm{i}}^{\mathrm{E}}(\mathrm{obs.}) - H_{\mathrm{i}}^{\mathrm{E}}(\mathrm{calc})\right\}^{2}}{(n-k)}\right]^{\frac{1}{2}} \tag{2}$$

are given in Table 2.

Table 1 Excess enthalpies H_m^E of cyclic ethers + MMTSO and cyclic ethers + 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) 1,4-dioxane + xMMTSO				
0.054065	91.09	0.38667	283.28	0.70096	214.38
0.055348	92.16	0.43277	286.28	0.70919	210.05
0.086895	132.13	0.45338	284.11	0.73753	190.75
0.14844	193.31	0.55629	269.13	0.79672	156.30
0.18721	220.92	0.55834	271.14	0.85025	116.01
0.18917	221.97	0.60514	258.14	0.93042	57.48
0.23801	248.83	0.64898	234.49	0.97632	20.28
0.31518	274.03	0.69693	216.01		
	(1 – x) 1,3-dioxane + xMMTSO				
0.052146	73.91	0.314488	252.83	0.807411	176.14
0.110314	136.62	0.376435	262.94	0.811523	170.16
0.115655	139.86	0.511667	262.80	0.827946	166.10
0.194451	200.55	0.609186	245.99	0.901126	110.11
0.222189	219.54	0.718283	219.50	0.955969	57.41
0.286202	247.33	0.753907	200.36		
	(1 – x) oxane + xMMTSO				
0.064768	244.76	0.340723	608.31	0.835849	308.71
0.133333	408.50	0.368916	629.25	0.847996	287.70
0.179649	486.25	0.410080	629.59	0.878269	392.94
0.194189	500.23	0.522029	625.63	0.910270	170.80
0.241801	553.69	0.657630	548.10	0.955110	84.98
0.315183	604.03	0.678348	529.22	0.966510	60.80
0.323371	605.78	0.783828	392.94		
	(1 – x) oxolane + xMMTSO				
0.02285	5.21	0.31489	66.36	0.73103	62.94
0.056912	13.35	0.36901	73.44	0.77917	57.08
0.092821	20.12	0.43776	78.26	0.78297	59.50
0.096290	22.63	0.49931	78.29	0.78685	57.69
0.09944	22.34	0.58738	75.21	0.86312	42.35
0.10640	26.11	0.60660	72.00	0.91376	30.43
0.14179	35.16	0.64591	70.25	0.97008	13.13
0.23807	52.74	0.71533	64.15		
0.24301	53.14	0.71728	64.07		

Table 1 Continued

x	H_m^E / J·mol^{-1}	x	H_m^E / J·mol^{-1}	x	H_m^E / J·mol^{-1}
($1-x$) 1,3-dioxolane + xMMTSO					
0.03472	38.92	0.40897	228.52	0.77352	136.36
0.07169	75.33	0.48214	229.68	0.77692	134.15
0.16483	145.56	0.55832	217.97	0.83342	105.25
0.25264	193.71	0.63732	196.02	0.91925	51.98
0.33519	220.87	0.70229	172.04	0.96545	24.45
($1-x$) 1,4-dioxane + xDMSO					
0.035283	46.89	0.45876	345.93	0.87792	157.11
0.070321	95.17	0.54808	346.79	0.90217	129.17
0.12286	154.32	0.64739	318.95	0.95612	62.42
0.16271	193.64	0.71054	289.92	0.98478	24.36
0.25180	268.11	0.77162	250.05		
0.35314	320.14	0.79518	231.18		
($1-x$) 1,3-dioxane + xDMSO					
0.03547	38.95	0.32562	320.67	0.70701	307.38
0.06920	75.36	0.40084	360.95	0.78542	237.67
0.14206	153.62	0.45010	375.14	0.82947	194.91
0.14413	164.78	0.51922	378.60	0.89520	127.48
0.18137	201.13	0.55036	370.99	0.95940	51.49
0.24081	256.26	0.63804	348.39	0.97923	24.71
($1-x$) oxane + xDMSO					
0.01250	68.36	0.38841	904.18	0.81637	543.79
0.03878	193.84	0.43176	925.25	0.84809	466.66
0.06306	302.65	0.45487	924.22	0.87954	386.14
0.12618	523.54	0.48312	925.18	0.89879	333.90
0.17026	639.87	0.53993	908.42	0.95738	150.19
0.24205	773.64	0.62814	840.01	0.96853	116.64
0.29359	842.39	0.68174	782.75		
0.37421	904.18	0.77819	625.31		
($1-x$) oxolane + xDMSO					
0.03308	41.25	0.24603	295.24	0.71774	399.51
0.04793	40.65	0.33290	375.95	0.81071	302.94
0.09617	120.16	0.41045	435.44	0.88452	197.48
0.12382	152.54	0.52542	469.55	0.93233	121.11
0.14544	177.56	0.56058	475.25	0.98352	30.48
0.19402	241.57	0.63138	455.55		

Table 1 Continued

x	H_m^E / J·mol^{-1}	x	H_m^E / J·mol^{-1}	x	H_m^E / J·mol^{-1}
	(1 – x) 1,3-dioxolane + xDMSO				
0.03197	15.82	0.39103	139.98	0.76705	122.08
0.06378	30.88	0.41306	143.59	0.80093	110.45
0.11966	56.82	0.50005	153.33	0.85015	90.03
0.13514	62.10	0.50499	153.59	0.88034	75.37
0.21868	93.74	0.60292	153.02	0.95145	34.02
0.31476	122.86	0.60744	152.70	0.97610	17.36
0.32027	126.94	0.70553	138.44		

All the excess enthalpies observed here were positive over the whole composition range at the temperature studied. As shown in Figs 1 and 2, the enthalpy of mixing of cyclomonoether, oxane, with MMTSO or DMSO showed the largest endothermic enthalpy. The excess enthalpies of the cyclodiethers, 1,3- and 1,4-dioxanes + MMTSO were less endothermic than that of the monoether, oxane, + MMTSO. This tendency obtained for the mixtures of MMTSO with mono- and diether of six-membered rings were obtained also for the corresponding DMSO mixtures. However, this sequence was not obtained for the mixtures of five-membered ring cycloethers with MMTSO, although it held for the mixtures with DMSO. The mixture of oxolane + MMTSO had the smallest endothermic excess enthalpy among the mixtures containing cycloethers studied in the present work. On the other hand, excess volumes of oxolane + MMTSO show the largest contraction on mixing among the cycloethers + MMTSO [9]. The contribution of enthalpic stabilization due to the largest volume contraction might be larger than those for other cycloether + MMTSO mixtures.

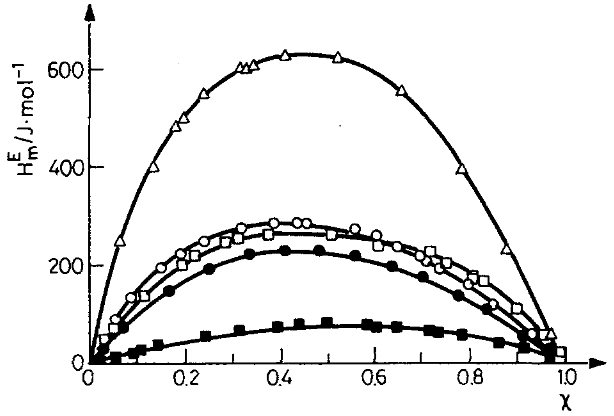

Fig. 1 Excess enthalpies of (1–x)cycloethers + xMMTSO at 298.15 K: O, 1,4-dioxane; □, 1,3-dioxane; Δ, oxane; ●, 1,3-dioxolane; ■, oxolane

Table 2 Coefficients A_i of Eq. (1) and the calculated standard deviations of the fit s_f

System		A_1	A_2	A_3	A_4	A_5	s_f / J·mol^{-1}
1,4-dioxane	+ MMTSO	1113.0	302.6	259.0	240.6		2.1
1,3-dioxane	+ MMTSO	1050.5	182.3	437.6	–129.1		1.9
oxane	+ MMTSO	2511.7	356.8	667.8	1056.1		1.9
oxolane	+ MTSO	310.33	5.04	–11.22	–132.96	51.00	1.3
1,3-dioxolane	+ MMTSO	904.78	234.15	29.39	5.2638		1.5
1,4-dioxane	+ DMSO	1393.4	63.37	95.42	–161.07		2.1
1,3-dioxane	+ DMSO	1519.6	–20.35	–366.54	–64.68		2.3
oxane	+ DMSO	3687.8	501.40	763.39	389.00	248.08	2.2
oxolane	+ DMSO	1870.0	–410.45	–321.08	104.41		2.2
1,3-dioxolane	+ DMSO	602.92	–50.44	123.71	–117.35	–129.75	2.0

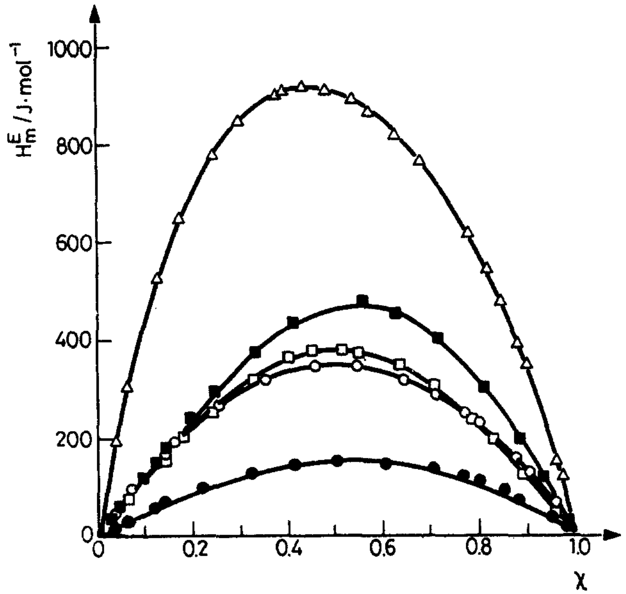

Fig. 2 Excess enthalpies of 1–x)cycloethers + xDMSO at 298.15 K: O, 1,4-dioxane; □, 1,3-dioxane; Δ, oxane; ●, 1,3-dioxolane; ■, oxolane

For the MMTSO mixtures, six-membered ring cycloethers gave more positive excess enthalpies, that is larger enthalpic destabilization than the five-membered ring cycloethers. The same result was obtained for the mixtures with DMSO, except that with oxolane.

In other words, enthalpic destabilization on mixing decreased with increasing number of ether oxygens in each cycloether molecule, except for oxolane + DMSO. Since the five-membered-ring cycloethers have larger ratios of molecular surfaces of polar oxygen atoms than the six-membered-ring ethers by about 20 per cent, the enthalpic destabilization due to the hindrance of dipolar interaction among the sulfoxides by insertion of nonpolar surfaces of the former cycloethers might be more decreased than the latter ones. Electrostatic stabilization between sulfoxide and ether radicals may be added to the above effect.

Because DMSO molecules have larger dipole moment ($\mu = 13.4 \times 10^{-30}$C·m) [10] than MMTSO ($\mu = 10.7 \times 10^{-30}$C·m) [11] in pure liquid state, the DMSO mixtures may exhibit larger positive enthalpies than MMTSO mixtures, owing to the insertion of nonpolar moieties of the ether molecules.

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies at infinite dilution were determined from Eq. (1) with the coefficients in Table 2, and are summarized in Table 3. There are complicated relations between the number of ether radicals and the excess partial molar enthalpies at infinite dilution. The latter values $H_1^{E,\infty}$ and $H_2^{E,\infty}$ were plotted in Fig. 3 against the number of methylene radicals between oxygen atoms in cycloether for the sake of understanding the effect on dipole-dipole interaction. Linear relationships were obtained as shown in Fig. 3 between the limiting excess partial molar enthalpies of the systems of the cycloethers + MMTSO or + DMSO at infinite dilution and the number of methylene radicals, $N(-CH_2-)$, of 1,3-dioxane, 1,4-dioxane and oxane except oxolane, if the number of 1,3-dioxane was counted as one in the place of three. This may show the effect of close localization of polar ether radicals upon intermolecular interactions between 1,3-dioxane and MMTSO. The limiting excess partial molar enthalpies of the cycloethers, $H_1^{E,\infty}$, of all the mixtures with MMTSO studied are longer than those of MMTSO, $H_2^{E,\infty}$, except for oxolane + MMTSO. Similar result had been obtained for the mixtures of methylbenzenes and MMTSO [7], although the mixtures of MMTSO with water [3], chloromethanes [4], and *n*-alkane-1-ols [6] were different.

Table 3 Limiting partial molar excess enthalpies $H_1^{E<\infty}$, and $H_2^{E<\infty}$ at 298.15 K

System	$H_1^{E<\infty}$ / kJ·mol^{-1}	$H_2^{E<\infty}$ / kJ·mol^{-1}
1,4-dioxane(1) + MMTSO (2)	0.83	1.92
1,3-dioxane(1)+MMTSO (2)	1.43	1.54
oxane(1)+MMTSO (2)	1.77	4.59
oxolane(1)+MMTSO (2)	0.48	0.22
1,3-dioxolane(1)+MMTSO (2)	0.69	1.17
1,4-dioxane(1)+DMSO (2)	1.58	1.39
1,3-dioxane(1)+DMSO (2)	1.24	1.07
oxane(1)+DMSO (2)	3.81	5.59
oxolane(1)+DMSO (2)	1.85	1.24
1,3-dioxolane+DMSO (2)	0.76	0.43

The limiting excess partial molar enthalpies of MMTSO in cycloether were increased by 1.0 kJ·mol^{-1} per methylene radical except for the mixture containing oxolane. Those of MMTSO in methylbenzenes were increased by 0.67 kJ·mol^{-1} per methyl radical [7]. The effect of methylene radicals in alicyclic molecules on the excess enthalpies were larger than that of methyl radicals in aromatic molecules. As we reported previously [2–7], the mixtures containing MMTSO are energetically less stable or more unstable than those containing DMSO, when the other component is polar, irrespective of being aprotic or protic, namely water [3], chloroform, deuterochloroform [5], dichloromethane [4], *n*-alkane-1-ols [6], and methyl alkylketones [12]. On the other hand, the mixtures containing DMSO, are more unstable than those with MMTSO, when the second component is nonpolar as $C_6H_{6-n}(CH_3)_n$, $n = 0$ to 3 [3, 7]. Although cycloethers have polar radicals, the mixture of cyclic ether + MMTSO and cyclic ether + DMSO showed a behaviour similar to the mixtures with nonpolar component. The major effect on the excess enthalpies of cycloether + MMTSO or + DMSO might arise from a hindrance of stable dipolar contacts by the non-polar radicals.

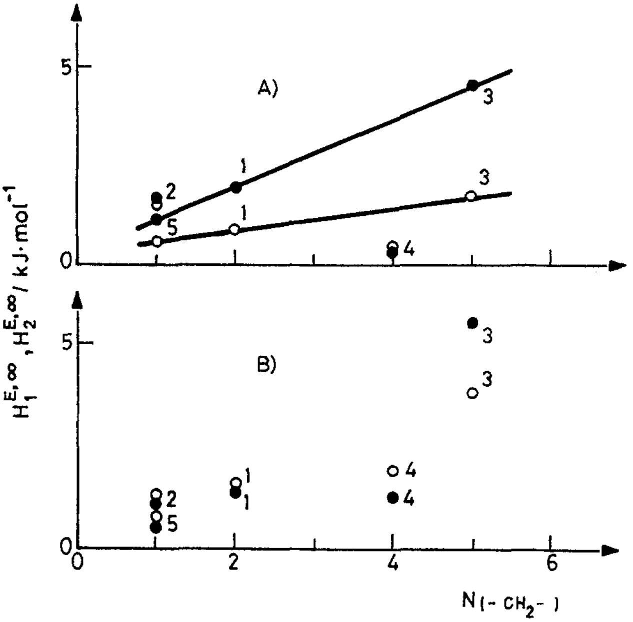

Fig. 3 Limiting excess partial molar enthalpies as a function of the number of methylene radicals between oxygen atoms: (A), cycloether(1) + MMTSO(2), (B) cycloether(1) + DMSO(2): O, $H_1^{E,\infty}$;●, $H_2^{E,\infty}$, 1, 1,4-dioxane; 2, 1,3-dioxane, 3, oxane; 4, oxolane; 5, 1,3-dioxolane

References

1 Thermodynamics of liquid mixtures containing methyl methyl-thiomethyl sulfoxide. IX.
2 T. Kimura and S. Takagi, J. Chem. Thermodyn., 18 (1986) 447.
3 T. Kimura and S. Takagi, Netsu Sokutei, 13 (1986) 2.
4 T. Kimura, T. Chanoki, H. Mizuno and S. Takagi, Nippon Kagaku Kaishi, 1986 (1986) 509.
5 T. Kimura and S. Takagi, Thermochim. Acta, 123 (1987) 293.
6 T. Kimura, T. Morikuni, T. Chanoki and S. Takagi, Netsu Sokutei, 17 (1990) 67.
7 T. Kimura, T. Tsuji, Y. Usui and S. Takagi, Thermochim. Acta, 163 (1990) 183.
8 T. Kimura and S. Takagi, J. Fac. Sci. Technol. Kinki Univ., 18 (1983) 49.
9 T. Kimura, S. Ebara, S. Segawa and S. Takagi, to be published.
10 E. M. Arnett and D. R. McKelvey, J. Amer. Chem. Soc., 88 (1966) 2598.
11 T. Kimura, Y. Toshiyasu and S. Takagi, to be published.
12 T. Kimura, N. Hirota and S. Takagi, to be published.

Zusammenfassung — Bei 298.15 K wurden die Überschußenthalpien von zehn binären Gemischen aus jeweils Methylmethylthiomethylsulfoxid (MMTSO) bzw. Dimethylsulfoxid (DMSO) mit einem der cyclischen Ether (Oxan, 1,3- und 1,4-Dioxan, Oxolan und 1,3-Dioxolan) bestimmt. Alle Gemische zeigen im gesamten Konzentrationsbereich eine positive Überschußenthalpie. Die Überschußenthalpien von Cycloether + MMTSO oder DMSO sinken mit zunehmender Anzahl der Sauerstoffatome im cyclischen Ether, mit Ausnahme von Oxolan + MMTSO. Die Überschußenthalpien für MMTSO + Cycloether sind kleiner als die für DMSO + entsprechender Cycloether, eine Ausnahme bilden die Gemische mit 1,3-Dioxolan.