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Excess enthalpies of diethylether, ethylpropylether, dipropylether + methyl methylthiomethyl sulfoxide or + dimethyl sulfoxide at 298.15 K [☆,1]

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Abstract

Excess enthalpies of six binary mixtures between methyl methylthiomethyl sulfoxide (MMTSO) or dimethyl sulfoxide (DMSO) and one of the dialkylethers (diethylether, ethylpropylether or dipropylether) have been determined at 298.15 K. All the mixtures observed showed positive excess enthalpies over the whole range of mole fractions and miscibility gaps. The mutual solubilities decreased with the increase in size of the alkyl radicals. Excess enthalpies determined at saturated mole fractions also decreased with the increase in size of the alkyl radicals. The enthalpies and entropies of transfer between conjugate mixtures were determined. The excess enthalpies of the mixtures containing DMSO were larger than those containing MMTSO. A comparison of the results with those for six binary mixtures containing a cyclic ether is made.

Keywords: Binary system; Dialkylether; DMSO; Excess enthalpy; Methyl methylthiomethyl sulphoxide; MMTSO

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[1] Thermodynamics of liquid mixtures containing methyl methylthiomethyl sulfoxide. Part X.

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1. Introduction

In our previous papers [1-7], 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 ($C_nH_{2n+1}OH$, $n = 1-9$), six methylbenzenes ($C_6H_{6-n}(CH_3)_n$, $n = 1-3$), and six cycloethers (1,3- and 1,4-dioxanes, oxane, oxolane, 1,3-dioxolane, oxepane) and those of DMSO with them were reported to determine the correlation between the thermodynamic properties of the mixtures and the molecular structures of their components.

In order to compare the excess enthalpies of the mixtures of cycloethers with those of some dialkylethers (diethylether, ethylpropylether and dipropylether), the present study has been carried out over the whole range of mole fractions.

2. Experimental

2.1. Materials

Purification procedures and the final purities of MMTSO (Nippon Soda Co.) and DMSO (Merck, uvasol) were the same as described previously [1,2]. Diethylether, ethylpropylether, and dipropylether (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. The GLC results obtained using respectively 2-m columns of 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with an FID on a Yanagimoto G180FP showed only some trace impurity peaks ($<10^{-7}$). The coulometric Karl-Fischer method on a moisturemeter (Mitsubishi Chemical Ind., CA-02) gave the water content of each sample as 0.01 mole% 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 fractions. Details of the calorimetric procedures [4,8] and the reproducibility test [8] of this calorimeter system are already described.

3. Results and discussion

The experimental results of the excess enthalpies obtained are summarized in Table 1 and plotted in Figs. 1 and 2. All the excess enthalpies observed were positive over the whole range of mole fractions at this temperature. The enthalpic unstabilization on mixing was not large, but all mixtures of dialkylether + MMTSO and dialkylether + DMSO showed two phase regions. Excess enthalpies for homogeneous mixtures of dialkylether + MMTSO and dialkylether + DMSO were fitted

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

x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})
$(1-x)$Diethylether + xMMTSO					
0.01879	86.50	0.31927	600.34	0.65863	738.25
0.04323	189.62	0.37145	629.19	0.65989	738.52
0.07681	318.78	0.37379	631.41	0.67089	718.11
0.08969	359.41	0.39795	632.05	0.74294	601.51
0.07730	316.11	0.41231	642.05	0.75425	580.92
0.13367	497.30	0.50207	679.12	0.76149	561.14
0.16063	537.29	0.52428	690.32	0.82517	426.20
0.17590	545.94	0.57462	713.11	0.83416	407.32
0.20213	555.79	0.60704	728.43	0.88414	292.64
0.26601	585.01	0.63554	742.45	0.97609	63.85
$(1-x)$Ethylpropylether + xMMTSO					
0.01187	68.01	0.15357	459.23	0.79478	515.70
0.01269	73.00	0.25946	462.83	0.81964	519.62
0.03793	204.89	0.30794	470.19	0.82752	520.04
0.04664	250.10	0.40935	479.26	0.87242	415.10
0.06513	331.69	0.55985	493.30	0.89431	360.01
0.08921	428.94	0.56463	493.95	0.92941	269.14
0.09018	435.62	0.65257	501.08	0.94326	212.46
0.09934	467.16	0.73071	506.13	0.96432	138.99
0.14279	454.86	0.73132	506.12	0.98597	56.68
0.14199	455.24	0.79441	514.67		
$(1-x)$Dipropylether + xMMTSO					
0.02960	135.97	0.19164	387.96	0.74190	379.31
0.05461	254.10	0.26643	385.96	0.81811	377.22
0.05546	257.76	0.36549	384.47	0.84254	377.35
0.08032	368.26	0.49029	382.59	0.85206	376.26
0.08381	389.32	0.58077	381.09	0.85225	376.16
0.12037	387.99	0.63683	380.32	0.86864	377.22
0.14935	388.11				
$(1-x)$Diethylether + xDMSO					
0.02525	119.85	0.28476	975.39	0.68354	943.04
0.04840	227.12	0.30474	1039.8	0.71418	875.12
0.10146	445.11	0.36675	1039.8	0.83271	565.33
0.12759	538.46	0.42379	1047.6	0.86312	470.33
0.15767	635.32	0.51154	1050.1	0.91197	311.69
0.17779	706.18	0.51867	1051.4	0.96012	144.92
0.23301	855.35	0.61115	1061.2	0.98171	67.52
0.24285	882.44	0.62460	1062.8		
0.26474	933.98	0.67832	951.04		
$(1-x)$Ethylpropylether + xDMSO					
0.01891	125.01	0.41093	659.37	0.96572	200.72
0.04268	292.66	0.64869	702.45	0.97043	172.58

Table 1 (continued)

x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})
0.04392	295.53	0.80096	727.85	0.97690	135.28
0.09036	588.09	0.84094	730.48	0.97767	135.52
0.09182	593.38	0.85318	739.36	0.97924	122.47
0.11025	609.52	0.88096	670.43	0.98328	99.13
0.13820	617.06	0.89247	612.47	0.99042	55.73
0.21628	629.61	0.89247	612.47	0.99290	43.84
0.33082	645.47	0.91654	480.11		
$(1-x)$Dipropylether + xDMSO					
0.02028	136.12	0.28477	499.95	0.84416	499.37
0.06277	375.73	0.33454	501.11	0.88105	502.22
0.07192	416.94	0.54621	504.21	0.89665	506.25
0.08209	465.64	0.56323	502.98	0.90777	469.22
0.08429	475.49	0.69008	499.49	0.91712	429.78
0.10703	497.57	0.71971	502.83	0.92392	405.97
0.14141	495.73	0.75671	500.39	0.95033	284.41
0.15009	498.33	0.79520	505.48	0.97102	173.73
0.22476	499.13	0.83358	499.96	0.98114	115.36

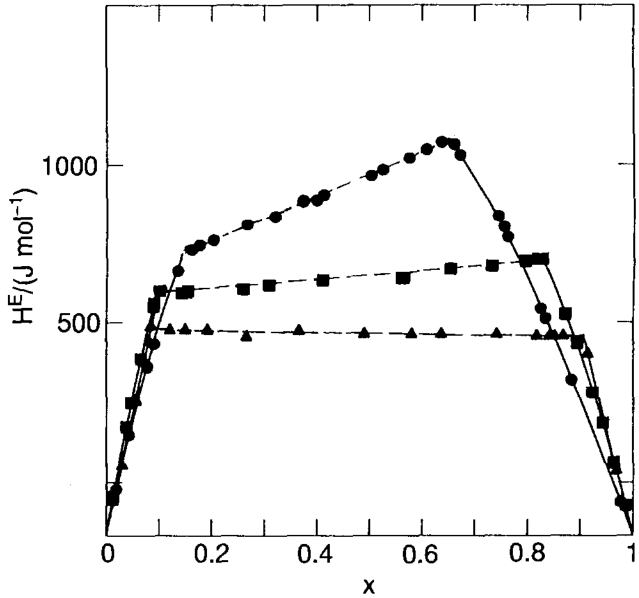

Fig. 1. Excess enthalpies of $(1-x)$dialkylether + xMMTSO at 298.15 K: ●, diethylether + MMTSO; ■, ethylproplyether + MMTSO; ▲, dipropylether + MMTSO.

with Eq. (1) using the method of least squares. The smoothed values are described as solid lines in Figs. 1 and 2. Excess enthalpies for heterogeneous mixtures

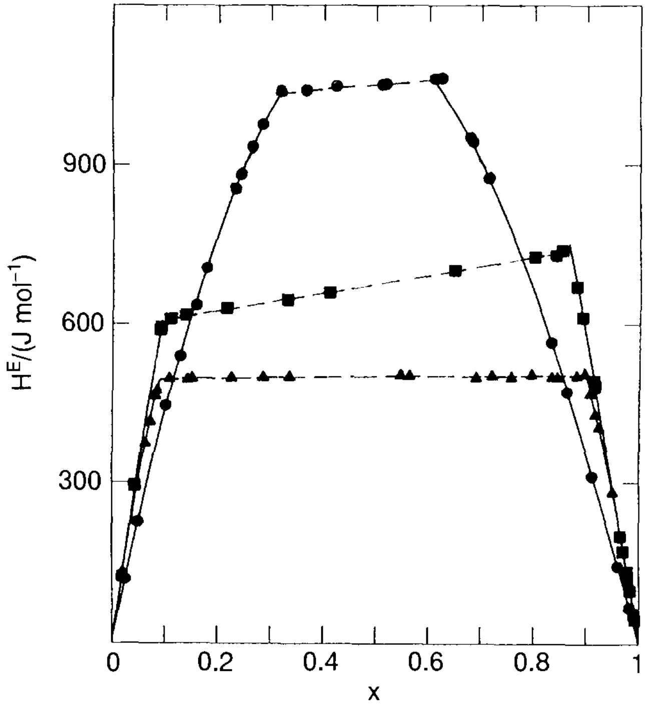

Fig. 2. Excess enthalpies of $(1-x)$dialkylether + xDMSO at 298.15 K: ●, diethylether + DMSO; ■, ethylpropylether + DMSO; ▲, dipropylether + DMSO.

were fitted with Eq. (2), and the calculated values are given as broken lines in Figs. 1 and 2.

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

$$H^E/\text{J mol}^{-1} = A_1 + A_2 x \tag{2}$$

where x denotes the mole fraction of MMTSO or DMSO in the mixtures. The coefficients A_i in Eqs. (1) and (2) and the standard deviations of the fits s_f

$$s_f = \left[\sum_{i=1}^{n} \{H^E(\text{obs}) - H^E(\text{calc})\}^2/(n-k)\right]^{1/2} \tag{3}$$

are given in Table 2.

The mixtures of dialkylether + MMTSO were the first systems to show a phase separation among the previously observed 28 mixtures with MMTSO [1–7]. The miscibility gap of dipropylether + MMTSO was the largest for the dialkylether mixtures of MMTSO. The excess enthalpies of heterogeneous mixtures for dipropylether + MMTSO was the lowest for mixtures of dialkylether + MMTSO. The features for dialkylether + DMSO were similar to those for the mixtures of MMTSO,

Table 2

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

Conc. region	Eq.	A_1	A_2	A_3	s_f/(J mol^{-1})
Diethylether + MMTSO					
$0.14 > x > 0.65$	(1)	3574.5	981.9	102.5	1.8
$0.14 < x < 0.65$	(2)	469.4	424.0		3.0
Ethylpropylether + MMTSO					
$0.05 > x > 0.90$	(1)	3596.4	881.00	1438.8	1.6
$0.05 < x < 0.90$	(2)	442.2	90.66		1.5
Dipropylether + MMTSO					
$0.05 > x > 0.90$	(1)	5700.4	381.14	−1449.3	1.4
$0.05 < x < 0.90$	(2)	390.4	−15.85		0.5
Diethylether + DMSO					
$0.14 > x > 0.65$	(1)	4581.9	585.6	−293.2	1.8
$0.14 < x < 0.65$	(2)	1014.8	73.96		2.0
Ethylpropylether + DMSO					
$0.05 > x > 0.90$	(1)	7287.9	475.8	−852.3	2.3
$0.05 < x < 0.90$	(2)	591.6	169.3		2.2
Dipropylether + DMSO					
$0.05 > x > 0.90$	(1)	3968.9	297.83	2805.1	2.0
$0.05 < x < 0.90$	(2)	497.8	5.29		2.1

but the enthalpic unstabilizations on mixing were larger than those for the each corresponding dialkylether mixture of MMTSO.

The mutual solubilities x(I) and x(II) of dialkylether + MMTSO and dialkylether + DMSO at 298.15 K were determined from the coefficients of Eqs. (1) and (2) and are listed in Table 3. The miscibility gaps were increased on increasing the size of the alkyl radicals in the dialkylethers. Excess enthalpies of the conjugate mixtures, $H^E(\mathrm{I})$ and $H^E(\mathrm{II})$, were determined at 298.15 K, where I and II refer to the saturated mixtures of the ether-rich and sulfide-rich phases, respectively. The observed heats of mixing q of the two phase regions may be given as

$$q = \frac{x(\mathrm{II}) - x}{x(\mathrm{II}) - x(\mathrm{I})} nH^E(\mathrm{I}) + \frac{x - x(\mathrm{I})}{x(\mathrm{II}) - x(\mathrm{I})} nH^E(\mathrm{II}) \tag{4}$$

by using the lever rule for partition of substances in liquid–liquid equilibrium, where n indicates the total amounts of the dialkylether and the sulfide in a mixture and x(I) and x(II) are the mutual solubilities of the sulfides in the mixture. Eq. (4) may be rearranged to

$$H^E = \frac{x(\mathrm{II})H^E(\mathrm{I}) - x(\mathrm{I})H^E(\mathrm{II})}{x(\mathrm{II}) - x(\mathrm{I})} + \frac{H^E(\mathrm{II}) - H^E(\mathrm{I})}{x(\mathrm{II}) - x(\mathrm{I})} x \tag{5}$$

This theoretical equation, Eq. (5), corresponds to the present empirical equation, Eq. (2). Therefore, $H^E(\mathrm{I})$ and $H^E(\mathrm{II})$ may be determined from Eq. (2) as

Table 3
Mutual solubilities, $x(\mathrm{I})$ and $x(\mathrm{II})$, and the excess enthalpies of conjugate mixtures of dialkylether + MMTSO and dialkylether + DMSO at 298.15 K

System	$x(\mathrm{I})$	$x(\mathrm{II})$	$H^E(\mathrm{I})/(\mathrm{J\ mol^{-1}})$	$H^E(\mathrm{II})/(\mathrm{J\ mol^{-1}})$
Diethylether + MMTSO	0.1428	0.6618	529.95	750.00
Ethylpropylether + MMTSO	0.09476	0.8234	450.83	516.89
Dipropylether + MMTSO	0.09064	0.9064	388.96	376.03
Diethylether + DMSO	0.3222	0.6070	1038.6	1059.7
Ethylpropylether + DMSO	0.0943	0.8686	607.56	738.65
Dipropylether + DMSO	0.0897	0.8986	498.27	502.55

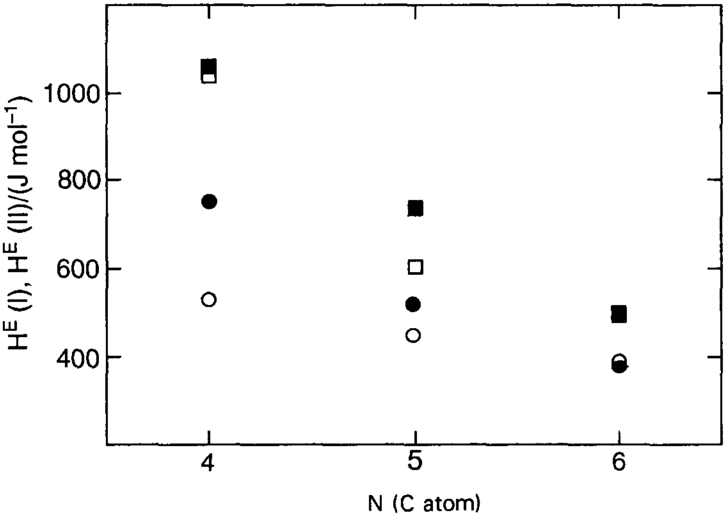

Fig. 3. Excess enthalpies of dialkylether-rich mixtures (mixture I) and excess enthalpies of sulfide-rich mixtures (mixture II) at 298.15 K in liquid–liquid equilibria. Circles and squares refer to the mixtures of MMTSO and DMSO, respectively. Filled and open symbols denote those for mixture I and mixture II, respectively.

$$H^E(\mathrm{I}) = H^E \tag{6}$$

when $x = x(\mathrm{I})$ and

$$H^E(\mathrm{II}) = H^E \tag{7}$$

when $x = x(\mathrm{II})$. The values of $H^E(\mathrm{I})$ and $H^E(\mathrm{II})$ are listed in Table 3 and are plotted in Fig. 3. Both the excess enthalpies of dialkylether-rich mixtures, $H^E(\mathrm{I})$, and those of sulfide-rich ones, $H^E(\mathrm{II})$, were decreased with an increase in the number of carbon atoms in the dialkylether molecules. This may result from the competition among (1) the decreasing number of strong dipolar contacts between sulfides, (2) the decreasing number of weak dipolar contacts between ether, and (3)

Table 4
Partial molar excess enthalpies (kJ mol^{-1}) of the conjugate mixtures of dialkylether + MMTSO or + DMSO at 298.15 K

System	H_1^E(I)	H_2^E(I)	H_1^E(II)	H_2^E(II)
Diethylether + MMTSO	0.13	2.94	1.70	0.24
Ethylpropylether + MMTSO	0.01	3.81	2.23	0.16
Dipropylether + MMTSO	0.00	4.67	4.06	0.00
Diethylether + DMSO	0.55	2.07	1.84	0.55
Ethylpropylether + DMSO	0.05	5.98	5.23	0.06
Dipropylether + DMSO	0.12	4.33	3.77	0.13

the formation of new dipole–dipole contacts and nonpolar contacts between the ethers and the sulfides, and the decreasing tendency of mutual solubilities with an increase in the number of carbon atoms in the ethers. Fig. 3 clearly indicates a decrease in the relative number of unfavorable contacts between unlike molecules with an increase in the number of carbon atoms of alkyl radicals in dialkylethers, corresponding to the decrease in mutual solubility.

For an elementary consideraton of the mutual solubility, the partial molar excess enthalpies at conjugate concentrations were determined from Eq. (1) with the coefficients in Table 2, and are summarized in Table 4. Here, H_1^E(I) and H_2^E(I) are respectively the partial molar excess enthalpies of the ether and the sulfide in the ether-rich mixtures. H_1^E(II) and H_2^E(II) are those of the ether and the sulfide in the sulfide-rich mixture, respectively.

As the partial molar Gibbs energy change between conjugate mixtures is zero, the enthalpy and entropy changes on transfer of each component were determined at the conjugate concentrations and are listed in Table 5.

The partial molar enthalpies of transfer of dialkylether were endothermic and those of MMTSO and DMSO were exothermic, accompanying the increase and decrease in partial molar entropy of transfer, respectively. This shows that the strong dipolar interaction may hinder the molecular motions in mixtures. Moreover, Table 5 shows that mixing of unsymmetric ethylpropylether and symmetric DMSO may cause a

Table 5
Thermodynamic functions of transfer of dialkylether(1) and MMTSO(2) or DMSO(2) from dialkyl-rich mixture(I) to sulfide-rich mixture(II) at 298.15 K

System	$\Delta_{trf}H_1$/ (kJ mol^{-1})	$\Delta_{trf}H_2$/ (kJ mol^{-1})	$\Delta_{trf}S_1$/ (JK^{-1} mol^{-1})	$\Delta_{trf}S_2$/ (JK^{-1} mol^{-1})
Diethylether + MMTSO	1.57	−2.71	5.27	−9.09
Ethylpropylether + MMTSO	2.22	−3.65	7.45	−12.2
Dipropylether + MMTSO	4.06	−4.67	13.6	−15.7
Diethylether + DMSO	1.29	−1.52	4.33	−5.10
Ethylpropylether + DMSO	5.18	−5.92	17.4	−19.9
Dipropylether + DMSO	3.65	−4.19	12.2	−14.1

Table 6
Limiting partial molar excess enthalpies $H_1^{\mathrm{E},\infty}$ and $E_2^{\mathrm{E},\infty}$ of dialkylether + MMTSO or + DMSO systems and those of cycloether + MMTSO or + DMSO systems [7,9] at 298.15 K

Systems	$H_1^{\mathrm{E},\infty}$/ (kJ mol^{-1})	$H_2^{\mathrm{E},\infty}$/ (kJ mol^{-1})	System	$E^{\mathrm{F}}\propto 1$/ (kJ mol^{-1})	$H_2^{\mathrm{E},\infty}$/ (kJ mol^{-1})
Diethylether(1) + MMTSO(2)	2.7_0	4.6_6	Oxolane(1) + MMTSO(2) [a]	0.48	0.22
Ethylpropylether(1) + MMTSO(2)	5.9_1	4.1_5	Oxane(1) + MMTSO(2) [a]	1.77	4.59
Diproplyether(1) + MMTSO(2)	3.8_7	4.6_3	Oxepane(1) + MMTSO(2) [b]	2.81	5.24
Diethyether(1) + DMSO(2)	4.8_7	3.7_0	Oxolane(1) + DMSO(2) [a]	1.85	1.24
Ethylpropylether(1) + DMSO(2)	5.9_5	6.9_1	Oxane(1) + DMSO(2) [a]	3.81	5.59
Dipropylether(1) + DMSO(2)	6.4_7	7.0_7	Oxepane(1) + DMSO(2) [b]	6.05	4.96

[a] Ref. 7. [b] Ref. 9.

particularly loose and unfavorable molecular packing in the mixture. However, unsymmetric MMTSO does not.

To compare the excess enthalpies obtained for the present dialkylether + sulfoxide mixtures with those for cyclic ether + sulfoxide mixtures, partial molar excess enthalpies at infinite dilution were determined from Eq. (1) with the coefficients in Table 2 and are summarized in Table 6, where those for cyclic ether + sulfoxide [7,9] are also summarized for comparison. These mixtures containing cyclic ethers do not show the miscibility gaps, but mix over the whole mole fraction range.

The pair of ethers on each line of Table 6 consist of the same number of carbon and oxygen atoms. Comparing each dialkylether with cyclic ether, the $H_1^{\mathrm{E},\infty}$ and $H_2^{\mathrm{E},\infty}$ values of mixtures containing diethylethers are a little larger than those containing cyclic ethers, except for $H_2^{\mathrm{E},\infty}$ of oxane and oxepane mixtures. This may arise from the weaker intermolecular interaction of dialkylethers than that of cyclic ethers (the molar volume of each dialkylether is larger than that of the corresponding cyclic one by about 25%, the enthalpy of evaporation is smaller, e.g., diethylether 26.5 and oxolane 35.0 kJ mol^{-1}, and the boiling point is also lower).

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