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論　文

Thermodynamics of Liquid Mixtures Containing Methyl Methylthiomethyl Sulfoxide, VI. Excess Enthalpies of (Methyl Methylthiomethyl Sulfoxide + Methanol, + Ethanol, + 1-Propanol) and (Dimethyl Sulfoxide + Methanol, + Ethanol, + 1-Propanol) at 298.15 K

Takayoshi Kimura*, Tomoko Morikuni, Takayuki Chanoki, Sadao Takagi*

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* Correspondence should be addressed to either T. K. or S. T.

Excess enthalpies of (methyl methylthiomethyl sulfoxide (MMTSO) + methanol, + ethanol, + 1-propanol) and (dimethyl sulfoxide (DMSO) + methanol, + ethanol, + 1-propanol) have been determined at 298.15 K. All the systems, except methanol + DMSO, show the positive enthalpies over the whole range of mole fraction. Excess enthalpies of MMTSO + alcohols are larger than those of DMSO + alcohols and increased with increasing the number of methylene groups of alcohols. Linear relationships are obtained between the excess partial molar enthalpies of MMTSO and DMSO at infinite dilution and relative dielectric constants of alcohols. These linearities also hold for the cases of aqueous mixtures of MMTSO and DMSO.

1. Introduction

In our previous papers,[1-4] excess thermodynamic functions of (methyl methylthiomethyl sulfoxide (MMTSO) + water, + benzene, + dimethyl sulfoxide (DMSO), + carbon tetrachloride, + chloroform, + dichloromethane, + deuterochloroform), (DMSO + water, + benzene, + deuterochloroform) and (chloroform + deuterochloroform) were reported.

In this paper, excess enthalpies of the mixtures between MMTSO and three alcohols and those between DMSO and the alcohols are determined over the whole range of mole fractions. Those results are compared with one another to clarify the correlation between thermodynamic properties of the mixtures and molecular structures of their components.

2. 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.[1,2] Methanol, ethanol (Merck, uvasol) and 1-propanol (Kishida, JIS-GR) were rectified over freshly activated molecular sieves 3A or 4A which had been evacuated at 423 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, 20 per cent PEG-1000 on celite 545 and Porapak Q with FID on Yanagimoto G180FP showed 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 mole per cent or less. All mixtures were prepared by mass.

Apparatus and procedures

A twin-microcalorimeter of heat-conduction type (laboratory designation MC-AII)[2,5,6] was used for the measurements of excess enthalpies at 298.15 K over the whole range of mole fraction. 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, i.d. 0.15 mm). A semimicrobalance (Mettler H20) was used in a thermostatted room. When the

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Department of Chemistry, Faculty of Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan

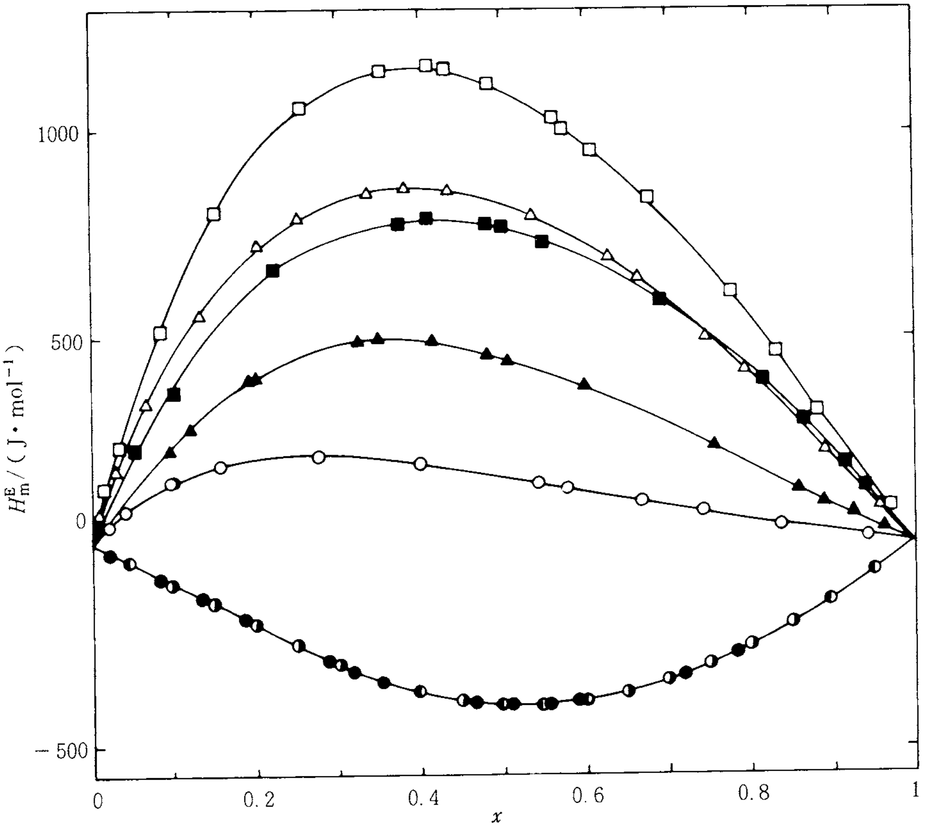

Fig. 1 Excess enthalpies at 298.15 K: ○, (1-x)methanol + xMMTSO; △, (1-x) ethanol + xMMTSO; □, (1-x)1-propanol + xMMTSO; ●, (1-x)methanol + xDMSO, this work; ◑, Quitzsch *et al.*[7]; ◐, superposed a point of Quitzsch *et al.* on one of the present work; ▲, (1-x)ethanol + xDMSO; ■, (1-x)1-propanol + xDMSO. Smoothed curves were calculated from Eqn. (1) with coefficients in Table 2.

mixing ratio of the two liquids was larger than 1.5 cm^3/0.2 cm^3, excess enthalpies were measured by successive dilution.

After thermal equilibrium was attained, mixing was started by slow rocking of the mixing vessels in mercury pools manually and completed by the tenth rocking. This procedure of slow locking was repeated at least three times until the heat change on stirring became constant within 0.1 per cent of it. The details of calorimetric procedures and reproducibility test of this calorimeter system were described elsewhere.[5,6]

3. Results and Discussion

Excess enthalpies

The experimental results of excess enthalpies obtained are summarized in Table 1 and Fig. 1. They were fitted with Eqn. (1) by the method of least squares.

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

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

$$s_f/(\mathrm{J\cdot mol^{-1}}) = [\sum_{i=1}^{n}\{H_i^E(\mathrm{obs})-H_i^E(\mathrm{calc})\}^2/(n-k)]^{1/2} \quad (2)$$

are given in Table 2.

All the excess enthalpies observed are positive over the whole range of mole fractions at this temperature, except the mixture of methanol + DMSO. Only the excess enthalpy of the system of methanol + DMSO are negative over the whole range of mole fraction. This result agrees with that of Quitzsch *et al.*[7] as shown in Fig. 1. The

Table 1 Experimental excess enthalpies at 298.15K

x	H^E / $J \cdot mol^{-1}$	x	H^E / $J \cdot mol^{-1}$
$(1\text{-}x)$methanol + xMMTSO			
0.02054	40.53	0.5432	146.4
0.04389	81.50	0.5788	133.4
0.09507	146.4	0.6694	101.9
0.09523	147.8	0.7412	76.18
0.1573	192.2	0.8391	43.14
0.2785	215.9	0.9426	13.74
0.4002	193.1		
$(1\text{-}x)$ethnol + xMMTSO			
0.01050	68.16	0.4348	848 3
0.03225	175.8	0.5377	785.1
0.03762	338.7	0.6311	684.5
0.09413	450.4	0.6650	641.0
0.1309	565.2	0.7484	507.9
0.2033	726.3	0.7951	426.2
0.2521	794.2	0.8905	231.9
0.3392	852.0	0.9588	86.01
0.3838	859.7		
$(1\text{-}x)$1-propanol + xMMTSO			
0.01896	132.1	0.5630	1032.4
0.03629	244.3	0.5735	1013.1
0.08694	522.5	0.6086	957.6
0.1544	802.7	0.6790	830.2
0.2595	1055.7	0.7766	608.6
0.3515	1145.2	0.8329	463.7
0.4144	1152.1	0.8844	324.5
0.4346	1150.2	0.9693	87.51
0.4854	1118.6		

x	H^E / $J \cdot mol^{-1}$	x	H^E / $J \cdot mol^{-1}$
$(1\text{-}x)$methanol + xDMSO			
0.02353	−21.51	0.4669	−386.2
0.04522	−44.21	0.4987	−390.4
0.08757	−85.52	0.5148	−391.0
0.1382	−139.9	0.5587	−391.1
0.1851	−189.9	0.5931	−384.7
0.2906	−289.6	0.5988	−382.1
0.3179	−311.0	0.7205	−325.1
0.3542	−336.1	0.7849	−270.2
0.3954	−360.0	0.8978	−145.1
0.4017	−360.8	0.9547	−69.18
$(1\text{-}x)$ethanol + xDMSO			
0.09564	224.9	0.5072	454.0
0.1247	278.1	0.6007	385.3
0.1932	383.5	0.7557	235.7
0.2044	398.4	0.8594	132.9
0.3267	486.8	0.8907	100.6
0.3495	493.5	0.9251	68.74
0.4164	492.0	0.9640	32.58
0.4842	466.0		
$(1\text{-}x)$1-propanol + xDMSO			
0.05811	228.3	0.5500	734.4
0.1019	381.1	0.6938	587.5
0.2235	648.5	0.8175	392.1
0.3530	768.1	0.8669	298.3
0.3746	775.1	0.9192	189.3
0.4842	768.3	0.9403	141.6
0.5008	763.4	0.9619	93.82

Table 2 Coefficients A_i of Eqn. (1) and the calculated standard deviation of the fit s_f

System	A_1	A_2	A_3	A_4	s_f / $J \cdot mol^{-1}$
Methanol + MMTSO	643.7	703.0	527.7	265.0	1.0
Ethanol + MMTSO	3256.8	1346.6	826.8	700.8	1.4
1-Propanol + MMTSO	4411.8	1888.8	636.4	330.0	2.1
Methanol + DMSO	−1562.4	220.6	327.1	127.0	0.9
Ethanol + DMSO	1835.8	1135.7	−43.19	−246.8	0.9
1-Propanol + DMSO	3047.0	922.9	516.9	135.2	1.3

Table 3 Coefficients B_i of Eqn. (3) and the calculated standard deviation of the fit s_f

System	B_1	B_2	B_3	B_4	B_5	s_f / J·mol^{-1}
Methanol + MMTSO	870.2	95.5	−148.5	41.57	–	1.5
Ethanol + MMTSO	3415.9	−2534.1	705.1	110.9	–	2.9
1-Propanol + MMTSO	4015.0	2884.3	1467.2	1124.2	602.4	2.4
Methanol + DMSO	−1364.7	1106.5	−266.6	18.41	–	1.0
Ethanol + DMSO	1922.1	743.0	−309.8	−204.5	–	1.0
1-Propanol + DMSO	3019.8	1054.5	598.8	19.02	–	1.5

excess enthalpies of mixtures of the alcohols with MMTSO are larger than those with DMSO by *ca.* 300 J·mol^{-1} at each maximum, except the case of methanol. Enthalpic unstabilization on mixing are increased with increasing the number of methylene groups of the alcohols.

In order to test the effect of molecular size, that is, molar volume in this case, the excess enthalpies were plotted in Fig. 2 against the volume fractions ϕ of MMTSO and DMSO and fitted with Eqn. (3) by the least squares method.

$$H^E/(\mathrm{J\cdot mol^{-1}})=(1-\varnothing)\ \varnothing\sum_{i=1}^{k}B_i\,(1-2\varnothing)^{i-1} \qquad (3)$$

Here, the volume fractions were calculated from molar volumes before mixing. The coefficients B_i and standard deviations of the fits are shown in Table 3. The best fitted curves for MMTSO + alcohol give maxima at ϕ = 0.5 ± 0.02. This shows that the asymmetries of excess enthalpy curves in Fig. 1 mainly arise from the differences in molecular size of the components. For the DMSO mixture, however, methanol, ethanol and 1-propanol show a minimum and maxima at ϕ = 0.65, 0.42 and 0.42, respectively. The curve for methanol + DMSO skews in DMSO-rich region, but those of ethanol + DMSO and 1-propanol + DMSO skew in alcohol-rich region. Excess enthalpies show that the mixture of methanol + DMSO is different from those of other two alcohols.

In our previous works, excess enthalpies of MMTSO mixtures and DMSO mixtures have same signs. Water,[2] chloroform, dichloromethane[3] and deuterochloroform[4] show exothermic mixing with the both sulfides. Benzene[2] and carbon tetrachloride[3] give endothermic mixing. However, in all the cases larger unstabilization or lesser stabilization in enthlapy is obtained on mixing with MMTSO. Unstabilization on mixing of methanol with MMTSO is also larger than that with DMSO, although they have opposite sign.

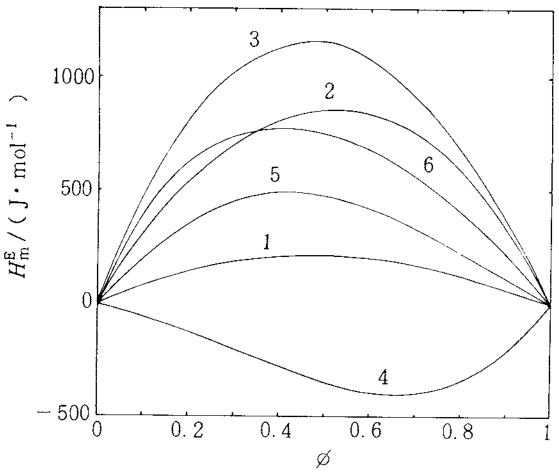

Fig. 2 Excess enthalpies at 298.15 K as a function of volume fractions: 1, (1-ϕ)methanol + ϕ MMTSO; 2, (1-ϕ)ethanol + ϕ MMTSO; 3, (1-ϕ)1-propanol + ϕ MMTSO; 4, (1-ϕ) methanol + ϕ DMSO; 5, (1-ϕ)ethanol + ϕ DMSO; 6, (1-ϕ)1-propanol + ϕ DMSO.

Excess partial molar enthalpies

Excess partial molar enthalpies were determined from Eqn. (1) and the coefficients listed in Table 2. They are plotted in Figs. 3 and 4. The excess partial molar enthalpy of DMSO H^E_2 of (methanol + DMSO) has a minimum at x_2 = 0.14 as shown in Fig. 4. The comparison of the

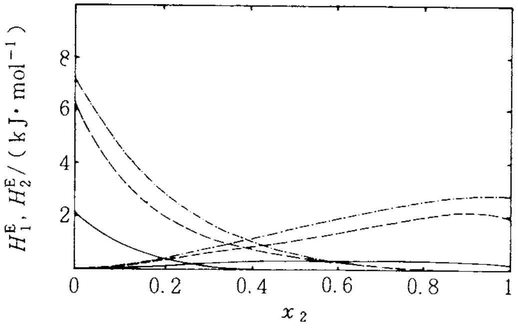

Fig. 3 Excess partial molar enthalpies of alcohol (1) and MMTSO(2) at 298.15 K: ———, methanol + MMTSO; – – – – , ethanol + MMTSO; —·—, 1-propanol + MMTSO.

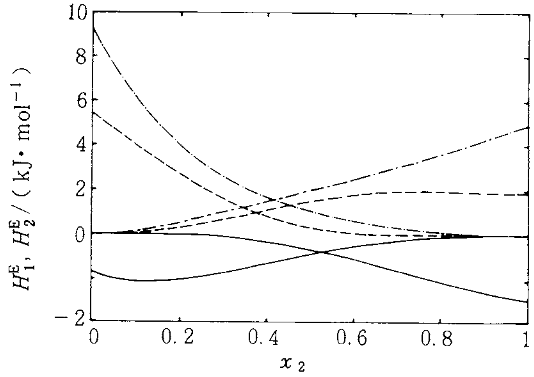

Fig. 4 Excess partial molar enthalpies of alcohol (1) and DMSO(2) at 298.15 K: ——— , methanol + DMSO; – – – – , ethanol + DMSO; ——·——, 1-propanol + DMSO.

Table 4 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}	ϵ_r[b]
Methanol(1) + MMTSO(2)	0.20	2.1	32.70[c]
Ethanol(1) + MMTSO(2)	2.0	6.1	24.55[c]
1-Propanol(1) + MMTSO(2)	2.8	7.3	20.45[d]
Water(10 + MMTSO(2)[a]	−0.91	−15	78.36[e]
Methanol(1) + DMSO(2)	−1.6	−0.89	32.70[c]
	−1.4[f]		
	−1.34[g]	−0.788[g]	
Ethanol(1) + DMSO(2)	0.90	2.7	24.55[c]
	1.2[f]		
1-Propanol(1) + DMSO(2)	2.5	4.6	20.45[d]
	2.5[f]		
Water(1) + DMSO(2)[a]	−4.9	−20	78.36[e]

[a] Reference 2.
[b] Relative dielectric constants of alcohols and water.
[c] Reference 10.
[d] Reference 11.
[e] Reference 12.
[f] Reference 9.
[g] Reference 7.

minimum of H_2^E of Quitzsch *et al.*⁷⁾ was obtained to be also x_2 = 0.14.

The excess partial molar enthalpies of MMTSO H_2^E of (alcohols + MMTSO) have maxima at higher mole fractions as shown in Fig. 3. They are x_2 = 0.65, 0.90 and 0.925 for methanol + MMTSO, ethanol + MMTSO and 1-propanol + MMTSO, respectively, shifting to higher mole fractions of MMTSO with increasing the number of methylene groups of alcohols. The excess partial molar enthalpies H_1^E and H_2^E of methanol + MMTSO in the range from 0.4 to 0.9 are almost constant. In this range, methanol or MMTSO molecules added into the mixture encounter nearly same energetic environment.

This may suggest the existence of some pseudo microscopic phase-separation which was supposed by Larkin[8].

Excess partial molar enthalpies at infinite dilution were calculated from Eqn. (1) with the coefficients in Table 2. They are summarized in Table 4, as well as literature values. Arnett and McKelvey[9] reported enthalpy of solution for the systems of alcohols + DMSO at the only one concentration of 5 x 10^{-3} mol·dm^{-3} at (298.2 ± 0.5) K. Their H_1^E for the system of 1-propanol + DMSO agreed completely with that of this work. However, their H_1^E for DMSO + methanol or ethanol were a little larger than the present values. Excess partial molar enthalpies of MMTSO at infinite dilution $H_2^{E,\infty}$ were larger than those of DMSO by *ca.* 3 ± 0.3 kJ·mol^{-1} for the same alcohols.

The excess partial molar enthalpies at infinite dilution $H_1^{E,\infty}$ and $H_2^{E,\infty}$ are plotted against relative dielectric constant ϵ_r of alcohols in Fig. 5 and compared with the aqueous mixtures[2]. The linear relationship was obtained between the excess partial molar enthalpies $H_2^{E,\infty}$ of each of MMTSO and DMSO at infinite dilution in the hydroxy compounds including water and the relative dielectric constants of the latters, as shown in Fig. 5 by each straight line. These relationships can be writen by

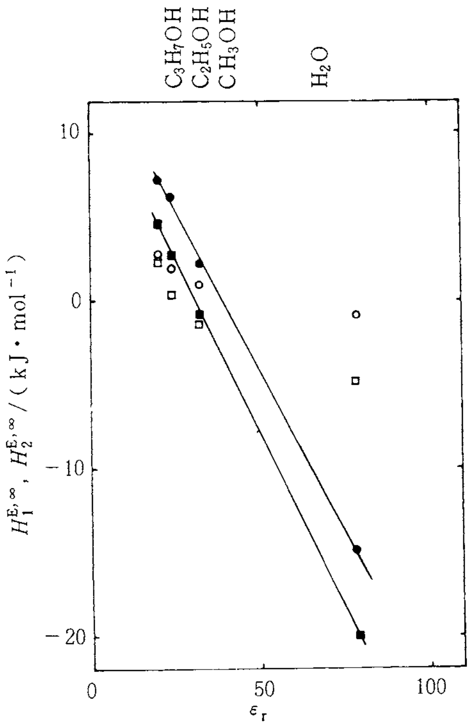

Fig. 5 Excess partial molar enthalpies at infinite dilution as a function of relative dielectric constants ϵ_r of alcohols and water: squares, (alcohol + MMTSO); circles, (alcohol + DMSO). $H_1^{E,\infty}$ and $H_2^{E,\infty}$ are represented by open and filled drawing, respectively.

$$H_2^{E,\infty}(\mathrm{MMTSO})/\mathrm{kJ\cdot mol^{-1}} = 15.2 - 0.386\epsilon_r, \quad s_f/\mathrm{kJ\cdot mol^{-1}} = 0.3 \tag{4}$$

$$H_2^{E,\infty}(\mathrm{DMSO})/\mathrm{kJ\cdot mol^{-1}} = 13.1 - 0.423\epsilon_r, \quad s_f/\mathrm{kJ\cdot mol^{-1}} = 0.1 \tag{5}$$

Enthalpic stabilization of the sulfoxides into the alcohols and water at infinite dilution become larger with the increase in relative dielectric constant of the solvents. The mixtures of MMTSO less stabilized than those of DMSO. This may reveal that the above linearities include implicitly the stabilization by hydrogen bonding between the hydroxy compounds and the sulfoxides[1−4].

The effect of dielectric constant of solvents on the system containing MMTSO is smaller than that of the system containing DMSO by a factor of about 0.9.

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