Netsu Sokutei **23** (2) 53-59

論　文

Excess Enthalpies of Binary Mixtures with Oxepane, Oxetane, 3,4-Dihydro-2*H*-pyrane, and Furan + Methyl Methylthiomethyl Sulfoxide and Dimethyl Sulfoxide at 298.15 K†

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Excess enthalpies of eight binary mixtures between each of methyl methylthiomethyl sulfoxide (MMTSO) and dimethyl sulfoxide (DMSO) and one of cycloethers (oxepane, oxetane, 3,4-dihydroxy-2*H*-pyrane and furan) have been determined at 298.15 K. All those mixtures show positive excess enthalpies over the whole range of mole fractions except furan + MMTSO, furan + DMSO, and oxetane + MMTSO. Excess enthalpies of the cycloether + MMTSO or + DMSO decrease with increasing the number of oxygen atoms in the cycloether molecules, except oxolane + MMTSO and increased with increasing methylene radicals in the ring. Excess enthalpies of MMTSO + cycloethers are smaller than those of DMSO + cycloethers for the same cycloether except the 1,3-dioxolane mixtures. The excess partial molar enthalpies at infinite dilution of mixtures of cycloethers +MMTSO and + DMSO were affected strongly by dipole-induced dipole interactions.

Introduction

In our previous papers,[1-9] excess thermodynamic functions for the binary mixtures of methyl methylthiomethyl sulfoxide (MMTSO) with water, benzene, dimethyl sulfoxide(DMSO), carbon tetrachloride, chloroform, dichloromethane, deutero-chloroform, n-$C_nH_{2n+1}OH$ (n=1 to 3) and six methylbenzenes $\{C_6H_{6-n}(CH_3)_n$, n=1 to 3$\}$, alkylether, halogenized aromatics, five cycloethers (1,3- and 1,4-dioxanes, oxane, oxolane and 1,3-dioxolane) and those of DMSO were reported.

In order to know further information between thermodynamic properties of the mixtures and molecular structures of their components, excess enthalpies of the mixtures between MMTSO and some cycloethers (oxepane, oxetane, 3,4-dihydro-2*H*-pyrane and furan) were determined over the whole range of mole fractions. Excess enthalpies of the cycloethers + DMSO were also determined as reference systems for the comparison.

Experimental

Materials

Procedures of purification and the final purities of MMTSO(Nippon Soda Co.) and DMSO (Merck, uvasol) are the same as those described previously,[2,3] oxepane (trimethyleneoxide), oxetane (hexamethylene oxide, Tokyo Kasei, GR), 3,4-dihydro-2*H*-pyrane and furan (Kishida, GR) were fractionally distilled over freshly activated molecular sieves 4A which had been evacuated at 453 K for 12h 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 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's method on a Moisturemeter (Mitsubishi Chemical Ind., CA-02) gave the water content of each

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†Thermodynamics of liquid mixtures containing methyl methylthiomethyl sulfoxide. XII.

sample to be 0.01 mole per cent or less.

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.[4, 10)]

Results and Discussions

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

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

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

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

are given in Table 2.

The excess enthalpies observed here were positive over the whole range of mole fractions at the temperature except furan + MMTSO and +DMSO. As shown in Fig. 1 and 2, the enthalpies of mixing of oxepane with MMTSO or DMSO showed the largest endothermic enthalpies. Oxetane + MMTSO and oxetane + DMSO showed the smallest endothermic enthalpies. Combining with previous results of cycloethers (oxane, 1,3- and 1,4-dioxane, oxolane, and 1,3-dioxolane) + MMTSO,[7)] excess enthalpies of the cycloethers + MMTSO increased with increasing the number of carbon atoms in their rings. In other words, the enthalpic destabilization on mixing was increased with increasing the number of methylene radicals in each cycloether molecule. Since the smaller-membered-ring cycloethers have larger ratios of molecular surfaces of polar oxygen atoms than the larger-membered-ring cycloethers, the enthalpic destabilisation due to hindering of dipolar interaction among the sulfoxides by insertion of nonpolar

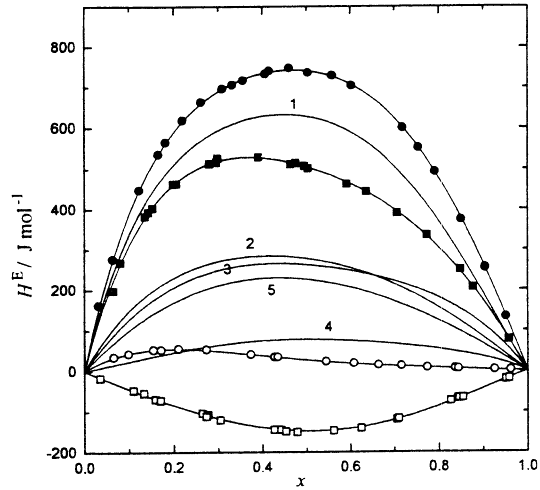

Fig. 1 Excess enthalpies of (1-x)cycloethers + xMMTSO at 298.15 K: ● , oxepane; ○ , oxetane; ■ , 3,4-dihydro-2*H*-pyrane; □ , furan; 1, 1,4-dioxane; 2, 1,3-dioxane; 3, oxane; 4, 1,3-dioxolane; 5, oxolane.

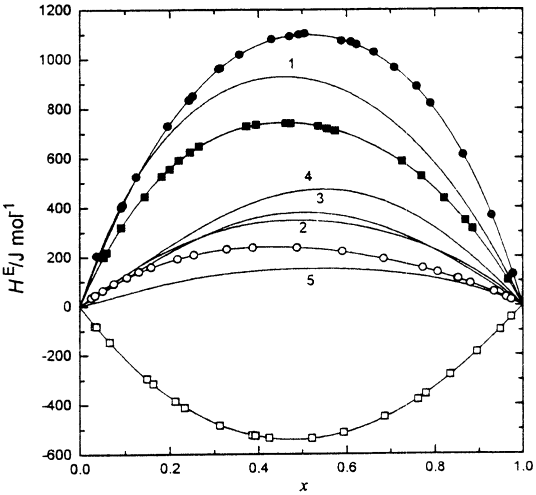

Fig. 2 Excess enthalpies of (1-x)cycloethers + xDMSO at 298.15 K: ● ,oxepane; ○ , oxetane; ■ , 3,4-dihydro-2*H*-pyrane; □ , furan; 1, 1,4-dioxane; 2, 1,3-dioxane; 3, oxane; 4, 1,3-dioxolane; 5, oxolane.

Table 1 Excess enthalpies H^{E} of cyclic ethers + MMTSO and cyclic ethers + DMSO at 298.15 K

x	$H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	x	$H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$
(1-x)oxetane + xMMTSO			
0.06581	33.86	0.54434	22.96
0.09933	42.40	0.60779	18.15
0.15475	51.59	0.66332	13.91
0.17201	52.32	0.71577	11.62
0.21048	54.33	0.77433	7.26
0.27306	52.56	0.83688	5.38
0.37385	40.53	0.84468	4.70
0.42758	34.58	0.92554	2.06
0.42758	34.58	0.96240	1.07
(1-x)oxepane + xMMTSO			
0.03244	160.63	0.46139	747.61
0.06376	276.17	0.50380	736.25
0.12348	447.48	0.55826	729.10
0.16634	535.57	0.55988	728.47
0.18252	564.57	0.60360	703.78
0.22025	618.29	0.71920	600.52
0.26200	662.84	0.75459	551.24
0.30949	696.14	0.79175	492.75
0.33231	705.35	0.85085	374.24
0.35722	716.76	0.90471	253.20
0.40700	732.35	0.90507	255.60
0.41626	740.15	0.95134	132.93
(1-x)furan + xMMTSO			
0.03570	-17.48	0.47799	-150.33
0.10940	-46.89	0.56114	-146.64
0.13271	-53.97	0.62384	-140.68
0.15874	-68.68	0.70539	-118.95
0.17007	-71.32	0.70998	-116.96
0.26384	-103.02	0.82624	-72.95
0.27690	-107.02	0.84314	-66.72
0.27289	-111.23	0.84386	-66.59
0.30418	-119.78	0.84541	-65.73
0.42676	-143.83	0.85417	-65.03
0.44118	-144.30	0.95090	-20.58
0.45281	-148.60	0.95816	-18.67

x	$H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$	x	$H^{\mathrm{E}}/\mathrm{J\cdot mol^{-1}}$
(1-x)3,4-dihydro-2*H*-pyrane + xMMTSO			
0.046611	168.34	0.46389	512.28
0.080490	268.27	0.47487	515.28
0.13581	382.83	0.49544	507.90
0.14240	392.66	0.50324	501.99
0.15270	403.15	0.59218	462.62
0.19829	462.46	0.63604	443.91
0.20574	463.15	0.70622	391.12
0.27963	513.34	0.77332	335.63
0.29560	516.65	0.84876	250.22
0.29822	526.38	0.87626	206.31
0.39098	529.63	0.95720	77.85
(1-x)oxetane + xDMSO			
0.02628	32.47	0.48874	236.35
0.03434	43.13	0.59130	219.79
0.05158	62.01	0.68541	190.22
0.07600	88.81	0.77318	151.46
0.10462	115.26	0.80700	134.22
0.13112	138.54	0.85266	108.71
0.15885	158.29	0.85398	108.51
0.21812	191.44	0.88185	88.00
0.25440	207.36	0.93472	52.73
0.32874	229.88	0.96293	31.49
0.38776	236.99	0.97386	21.52
(1-x)oxepane + xDMSO			
0.03810	204.28	0.42979	1079.75
0.09197	400.75	0.47123	1090.43
0.09502	409.98	0.49286	1098.09
0.12531	523.98	0.50557	1102.35
0.19513	729.19	0.58802	1071.60
0.24254	832.23	0.61023	1068.62
0.25117	849.24	0.62323	1056.27
0.30998	959.34	0.66294	1025.68
0.31378	962.27	0.70921	964.04
0.35695	1016.67	0.75854	885.90

Table 1 -continued

x	$\frac{H^{\mathrm{E}}}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H^{\mathrm{E}}}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H^{\mathrm{E}}}{\mathrm{J\cdot mol^{-1}}}$	x	$\frac{H^{\mathrm{E}}}{\mathrm{J\cdot mol^{-1}}}$
0.79006	817.64	0.92914	364.89	(1-x)3,4-dihydro-2*H*-pyrane + xDMSO			
0.8641	612.62	0.97834	126.19	0.052633	200.54	0.46126	741.16
				0.058863	218.12	0.47319	741.65
(1-x)furan + xDMSO				0.090863	320.41	0.53517	729.25
0.03329	-80.46	0.42430	-535.04	0.14390	445.63	0.55466	720.05
0.03686	-81.07	0.52209	-536.76	0.18176	526.30	0.57308	711.30
0.06640	-145.24	0.59278	-513.23	0.19934	555.20	0.72577	585.34
0.14890	-293.24	0.68612	-448.66	0.21946	591.11	0.76902	524.62
0.16250	-314.39	0.76142	-379.82	0.24398	625.38	0.82082	435.22
0.21203	-385.11	0.77919	-355.89	0.26458	649.12	0.86973	346.08
0.23323	-411.59	0.83434	-279.51	0.37172	729.43	0.88554	312.59
0.31206	-483.65	0.89507	-187.36	0.37285	729.34	0.96603	102.24
0.38523	-523.25	0.94812	-98.37	0.39421	735.24		
0.39313	-526.35	0.97343	-47.56				

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

System	A_1	A_2	A_3	A_4	A_5	$\frac{s_f}{\mathrm{J\cdot mol^{-1}}}$
oxetane + MMTSO	106.77	201.16	235.39	122.54		0.6
oxepane + MMTSO	2962.9	232.52	1016.1	983.97	45.66	2.3
furan + MMTSO	-590.11	35.14	161.25	-65.82		2.1
3,4-DHP[a] + MMTSO	2021.3	638.4	1038.5	508.1		2.6
oxetane + DMSO	946.39	237.5	151.97	-10.69		1.1
oxepane + DMSO	4390.5	-141.0	1117.3	-410.60		3.2
furan + DMSO	-2161.0	-169.7	-105.4	-96.55	144.36	2.3
3,4-DHP[a] + DMSO	2961.1	383.3	746.6	134.5		2.7

[a] 3,4-dihydro-2*H*-pyrane

surfaces of the cycloethers might be larger than the latter ones. Stabilization due to dipole-dipole and dipole-induced dipole interactions between sulfoxide and ether radicals might be added to the above effect. Excess enthalpies of furan + MMTSO and furan + DMSO were relatively small but negative over the whole range of mole fraction. However, since those mixtures showed larger volume contraction on mixing[11] than another cycloether + MMTSO and + DMSO at 298.15 K, those negative enthalpies for the furan mixtures might arise by the effect of enthalpic stabilization due to volume contraction.

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies at infinite dilution were determined from Eqn.(1) with the coefficients in Table 2, and summarised in Table 3. There were complicated relations between the number of ether radicals or of carbon atom of cyclic ether ring and the excess partial molar enthalpies at infinite dilution.

The mixtures of halogenized benzene + MMTSO or + DMSO showed strong effect of dipole-dipole interaction upon excess partial molar enthalpies at infinite dilution.[9] In order to know the effect of dipole-dipole interaction on excess partial molar enthalpies at infinite dilution of cycloethers + MMTSO or + DMSO,the dipole-dipole interaction energy u_{12}(D-D) expressed as an equation(3)[15] were estimated.

$$u_{12}(\mathrm{D-D}) = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{r^6kT} \qquad (3)$$

The interaction energy due to dipole-dipole interaction is proportional to the square of dipole moment μ of each component and in inverse proportion to r^6 from eqn. (3). The r^6 might be proportional to square of volume when molecules are approximately sphere. $H_1^{E,\infty}$ and $H_2^{E,\infty}$ for cycloether + MMTSO or +DMSO of this work and those reported previously[8], were plotted in Fig. 3 against square of dipolemoment of cycloether devided square of molar volume of cycloether. The dipole moments of cycloethers which could not be found were calculated by Nemesis(ver 2.0, Oxford Molecular Ltd 1994). The calculated dipole moments were compared with observed ones in Table 4. Fig. 3 showed complicate correlation between dipole-dipole interaction energy and limiting excess enthalpies of cycloether and those of sulfoxides. It might be small dipole-dipole interaction effect on the excess enthalpies of the cycloether mixtures. On the other hand, dipole-induced dipole interaction energy u_{12}(D-ID) is also expressed as an equation (4); [15]

$$u_{12}(\mathrm{D-ID}) = \frac{\alpha_2\mu_1^2 + \alpha_1\mu_2^2}{r^6} \qquad (4)$$

Here α is the polarizability of cycloether, MMTSO and DMSO. In order to understand the effect of dipole-

Table 3 Limiting partial molar excess enthalpies and at 298.15 K

System	$H_1^{E,\infty}$ / kJ·mol^{-1}	$H_2^{E,\infty}$ / kJ·mol^{-1}
oxetane(1) + MMTSO(2)	0.019	0.67
oxepane(1) + MMTSO(2)	2.81	5.24
3,4-DHP[a](1)+ MMTSO(2)	1.91	4.21
furan(1) + MMTSO(2)	-0.398	-0.460
oxetane(1) + DMSO(2)	0.87	1.33
oxepane(1) + DMSO(2)	6.05	4.96
furan(1) + DMSO(2)	-1.86	0.39
3,4-DHP[a](1) + DMSO(2)	3.19	4.23

a 3,4-dihydro-2*H*-pyrane

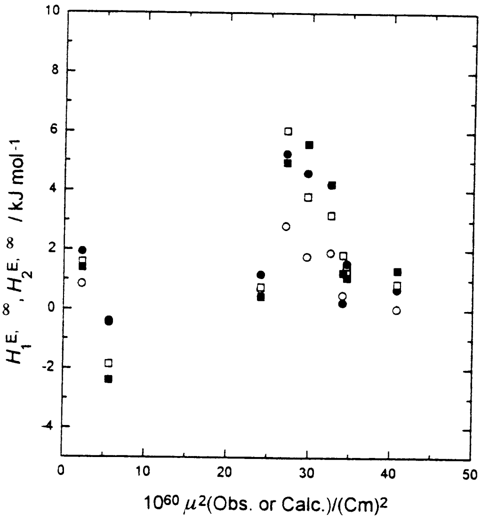

Fig. 3 Relation between limiting excess partial molar enthalpies and squares of dipole moments of the cycloethers. Symbols of circles and squares are the mixtures of cycloethers(1) + MMTSO(2) and those of cycloethers(1) + DMSO(2), respectively. Open and solid marks show $H_1^{E,\infty}$ and $H_2^{E,\infty}$, respectively.

Table 4 Comparison of obsereved and calclated dipolemoments of cycloethers

cycloether	$\frac{10^{30}\mu(\mathrm{obs})}{(\mathrm{Cm})^2}$	$\frac{10^{30}\mu(\mathrm{obs})}{(\mathrm{Cm})^2}$
oxetane	- - -	6.38
oxepane	- - -	5.21
3,4-DHP	- - -	5.71
furan	2.37[16)]	3.44
1,4-dioxane	1.50[17)]	0
1,3-dioxane	- - -	5.88
oxane	5.44[18)]	5.38
oxolane	5.85[19)]	5.44
1,3-dioxolane	4.91[19)]	4.88

a 3,4-dihydro-2*H*-pyrane

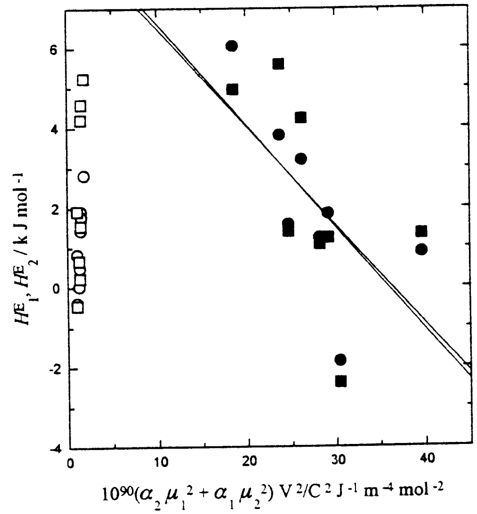

Fig. 4 Correlation of limiting excess partial molar enthalpies and stabilisation energy of dipole-induced dipole interaction between the cycloethers and the sulfoxides. Symbols of circles and squares are the mixtures of cycloethers(1) + MMTSO(2) and those of cycloethers(1) + DMSO(2), respectively. Open and solid marks show $H_1^{E,\infty}$ and $H_2^{E,\infty}$, respectively.

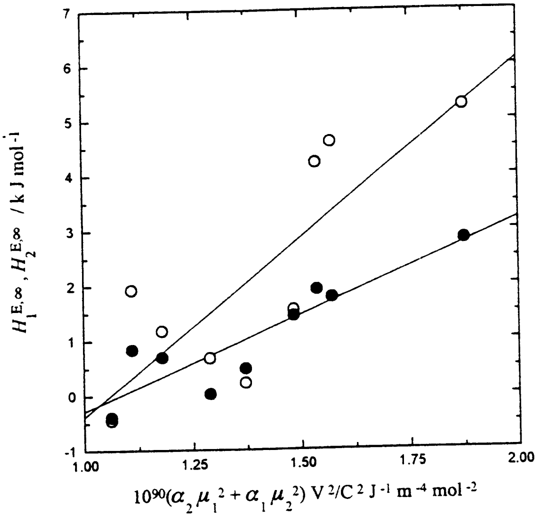

Fig. 5 Relation between limiting excess partial molar enthalpies and stabilisation energies of dipole-induced dipole of the cycloethers and MMTSO. Open and solid marks show $H_1^{E,\infty}$ and $H_2^{E,\infty}$, respectively.

Table 5 The coefficents of eqn.(5)

System		a	$10^{-90}b$	$\frac{s_f}{\mathrm{J\cdot mol^{-1}}}$
cycloether+ MMTSO	$H_1^{E,\infty}$	-3.76	3.47	0.4
	$H_2^{E,\infty}$	-6.87	6.49	1.2
cycloether + DMSO	$H_1^{E,\infty}$	9.19	-0.256	1.6
	$H_2^{E,\infty}$	8.97	-0.247	2.1

induced dipole interaction on the system, $H_1^{E,\infty}$ and $H_2^{E,\infty}$ of cycloether + MMTSO and +DMSO were plotted in Fig. 4 against u_{12}(D-ID). Fig. 4 showed a good relation between the limiting excess enthalpies of cycloether + DMSO and dipole-induced dipole interaction. However, there is no clear relation for the systems of cycloether + MMTSO. The relations between the limiting excess enthalpies of cycloether + DMSO and stabilization energy of dipole-induced dipole interaction were negative correlations for the system of cycloether + DMSO, the stabilization energy of dipole-induced dipole interaction increased with decreasing enthalpic unstabilization on mixing for the system of cycloether

+ DMSO. Coefficients of linear relation(Eqn. 5) between limiting excess enthalpies and the stabilization energies of dipole-induced dipole interaction

$$H_i^{E,\infty}/\mathrm{kJ\ mol^{-1}} = a + b(\alpha_2\mu_1^2+\alpha_1\mu_2^2)/V^2 \qquad (5)$$

by the least squares fitting were listed in Table 5. The stabilization energies of dipole-induced dipole interaction of the systems of cycloether + MMTSO were lower than 10 per cent of those of cycloether + DMSO.

Since DMSO molecules have larger dipolemoment (=13.4 × 10^{-30} Cm)[12] than MMTSO(=10.7 × 10^{-30} Cm)[13] in pure liquid state, the effect of stabilization energies of induce-dipole interaction were small for the mixtures containing MMTSO. Those relation of cycloether + MMTSO were also plotted in Fig. 5 to clearfy the relation. The limiting excess enthalpies of cycloether and MMTSO increased with increasing stabilization energy of dipole-induced dipole interaction of cycloether + MMTSO. The major effect on the excess enthalpies of cycloether + MMTSO or + DMSO might arise from hindering of stable dipolar contacts by the non-polar radicals and stabilization of dipole-induced dipole interaction. Since the cycloethers have little polar radicals, the mixtures described here might show the behaviour similar to the mixtures of nonpolar components with MMTSO and DMSO.

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要旨

メチルメチルチオメチルスルホキシド (MMTSO) およびジメチルスルホキシド (DMSO) とシクロエーテル (オキセパン，オキセタン，3,4-ジヒドロ2-*H*-ピランおよびフラン) との全濃度範囲での混合エンタルピーを298.15 Kで測定した。フラン+MMTSO，およびフラン+DMSO以外の系では混合エンタルピーは正の値を示した。MMTSOを含む系ではオキソラン系を除いてエーテル基の増加と共に不安定化は減少したがヘテロ環中のメチレン基の増加と共に不安定化は増加した。1,3-ジオキソラン系を除いてMMTSO系はDMSO系よりも不安定化が小さい。シクロエーテルとMMTSO系およびDMSO系は双極子ー誘起双極子相互作用が大きいことを示した。