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Thermodynamics of liquid mixtures containing methyl methylthiomethyl sulfoxide

XVI. Excess enthalpies of some alkylbenzenes+methyl methylthiomethyl sulfoxide and alkylbenzenes+dimethyl sulfoxide at 298.15 K

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Abstract

Excess enthalpies of binary mixtures between one of the alkylbenzenes (ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, *n*-pentylbenzene, *n*-hexylbenzene, *n*-heptylbenzene and *n*-octylbenzene) and methyl methylthiomethyl sulfoxide (MMTSO) or dimethyl sulfoxide (DMSO) have been determined at 298.15 K. For all the mixtures, changes in enthalpy are positive over the whole range of mole fractions. Linear relationships are obtained between the limiting excess partial molar enthalpies $H_1^{\mathrm{E},\infty}$ and $H_2^{\mathrm{E},\infty}$ and $(\alpha_2\mu_1^2+\alpha_1\mu_2^2)V_1^{-1}V_2^{-1}$, where α and μ are the polarizabilities and electric dipole moments of the alkylbenzenes(1) and the sulfoxides(2), respectively, and V the molar volumes of 1 or 2. Phase separations are observed for the binary mixtures containing alkylbenzenes higher than *n*-butylbenzene. Mutual solubilities determined are decreased with increase of sizes of alkyl radicals. In homogeneous regions, all the molar excess enthalpies are increased with increase of the size of alkyl radicals.

Keywords: Excess enthalpy; Binary mixtures; Methyl methylthiomethyl sulfoxide; Dimethyl sulfoxide; Alkylbenzene

1. Introduction

In our previous papers [1–13], 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-$C_nH_{2n+1}OH$, $n=1$–9), six methylbenzenes $\{C_6H_{6-n}(CH_3)_n$, $n=1$–$3\}$, six cycloethers, three alkylethers, eleven halogenated aromatics, and five alkyl cyanides and those of DMSO were reported.

In order to obtain further information regarding thermodynamic properties of the mixtures and molecular structures of their components, particularly a comparison of the above correlations with those of the mixtures of six methylbenzenes, excess enthalpies of the mixtures of MMTSO and some alkylbenzenes (ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, *n*-pentylbenzene, *n*-hexylbenzene, *n*-heptylbenzene and *n*-octylbenzene) were determined over the whole range of mole fractions. Those of alkylbenzene + DMSO were also determined as the reference systems.

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2. Experimental

2.1. Materials

Procedures of purification and the final purities of MMTSO (Nippon Soda) and DMSO (Cica-Merck, uvasol) were the same as described previously [1,2]. Ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, *n*-pentylbenzene, *n*-hexylbenzene, *n*-heptylbenzene and *n*-octylbenzene (Kishida, GR) were fractionally distilled over freshly activated molecular sieves 4A which had been evacuated at 453 K for 12 h under 10^{-2}–10^{-3} Pa. G.l.c. results obtained by using each 2 m column of 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with FID Yanagimoto G180FP showed merely some trace-impurity peaks ($<10^{-7}$). Coulometric Karl–Fischer's method on a moisturemeter (Mitsubishi Chemical, CA-02) gave the water content of each sample at 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 K over the whole range of mole fractions. The details of calorimetric procedures and reproducibility test of this calorimeter system were described elsewhere [2,4,14].

3. Results and discussion

The experimental results of excess enthalpies obtained are summarized in Table 1 and plotted in

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

x	$H^E/(\mathrm{J\ mol^{-1}})$	x	$H^E/(\mathrm{J\ mol^{-1}})$	x	$H^E/(\mathrm{J\ mol^{-1}})$
(1 − x)Ethylbenzene + xMMTSO					
0.01859	91.99	0.30611	750.48	0.84484	406.33
0.02593	124.10	0.39874	758.59	0.88565	315.84
0.04781	217.14	0.46017	790.19	0.89224	303.66
0.08436	353.39	0.56017	755.33	0.93302	200.01
0.13596	502.91	0.64629	697.82	0.97710	70.92
0.17951	597.94	0.74556	579.84	0.98605	44.11
0.22218	668.16	0.80721	483.32		
(1 − x)n-Propylbenzene + xMMTSO					
0.02441	143.16	0.24814	825.47	0.78815	667.07
0.05620	298.31	0.31361	896.65	0.82748	575.65
0.11210	516.03	0.41283	956.86	0.88372	415.59
0.15536	642.58	0.48462	967.59	0.91832	305.53
0.17877	697.91	0.58615	936.37	0.94682	206.07
0.21751	773.69	0.68883	840.18	0.98207	71.92
(1 − x)n-Butylbenzene + xMMTSO					
0.01674	111.18	0.27026	968.65	0.83819	641.26
0.02825	185.10	0.35049	1038.9	0.88156	514.19
0.05236	322.51	0.48380	1057.2	0.90679	425.08
0.07264	420.58	0.57603	1021.3	0.94296	279.56
0.11648	604.43	0.63166	981.78	0.95502	226.41
0.15853	743.93	0.73168	862.32	0.99126	47.16
0.21993	887.45	0.79999	734.89		
(1 − x)n-Pentylbenzene + xMMTSO					
0.02825	195.76	0.31643	903.47	0.67999	750.69
0.09149	526.18	0.33069	897.52	0.72246	733.33
0.13238	685.91	0.37401	888.89	0.75162	721.53
0.16417	782.69	0.43485	879.86	0.79122	671.53
0.18444	831.11	0.45176	871.53	0.81142	652.44
0.19212	846.22	0.50648	847.92	0.81910	633.80

0.22577	908.72	0.55364	827.08	0.84931	564.55
0.23713	896.68	0.59035	800.69	0.89885	425.25
0.24802	918.06	0.64507	783.33	0.91301	373.38
0.26170	912.50	0.64580	766.84	0.95551	212.93
0.29194	912.50	0.66775	765.28	0.97839	112.86
(1 − x)n-Hexylbenzene + xMMTSO					
0.01279	103.58	0.33373	774.09	0.85911	573.32
0.04552	335.25	0.35191	762.51	0.86733	553.36
0.05909	420.85	0.54755	657.87	0.89089	488.31
0.09273	594.13	0.65582	594.31	0.91884	349.78
0.11648	694.94	0.69764	575.79	0.94075	307.31
0.16315	808.27	0.73946	554.72	0.95920	227.05
0.18465	844.43	0.79703	516.89	0.98897	68.68
0.24772	811.13	0.82277	504.24		
0.29224	790.07	0.84457	500.11		
(1 − x)n-Heptylbenzene + xMMTSO					
0.02644	211.79	0.41193	625.79	0.95638	275.57
0.05257	376.22	0.68328	498.30	0.97501	169.59
0.08969	546.69	0.81803	369.16	0.98708	87.96
0.12627	655.19	0.90793	274.56	0.99006	72.38
0.28169	649.94	0.93058	210.43		
(1 − x)n-Octylbenzene + xMMTSO					
0.00563	54.40	0.09096	530.84	0.86371	282.56
0.01224	116.61	0.11845	590.13	0.93149	200.97
0.01468	138.66	0.16579	587.05	0.97386	172.20
0.02431	220.95	0.17738	609.12	0.98314	116.15
0.03716	319.96	0.29534	568.10	0.98912	77.38
0.05860	455.63	0.43936	511.53	0.99681	23.15
0.07378	533.53	0.69656	402.82		
0.08305	573.60	0.84073	292.28		
(1 − x)n-Ethylbenzene + xMMTSO					
0.03201	155.20	0.31827	880.84	0.91351	424.03
0.04586	210.88	0.44602	980.12	0.92859	363.19
0.08869	375.35	0.54502	1000.3	0.95756	228.78
0.13944	538.07	0.62841	980.93	0.98467	90.69
0.17899	645.12	0.73288	879.66	0.98815	68.59
0.21579	720.05	0.82636	700.19		
0.22180	730.51	0.87226	570.21		
(1 − x)n-Propylbenzene + xMMTSO					
0.01438	93.69	0.37083	1150.9	0.87194	655.71
0.04115	252.93	0.42597	1185.4	0.91351	482.20
0.06468	380.05	0.50041	1204.1	0.92451	430.31
0.08926	490.96	0.55946	1192.3	0.96020	246.39
0.15294	733.95	0.66363	1121.3	0.98991	66.59
0.19259	855.03	0.73462	1024.0		
0.26175	1005.9	0.80076	875.35		
(1 − x)n-Butylbenzene + xMMTSO					
0.03154	225.42	0.27074	1110.6	0.84459	873.04
0.04635	320.58	0.31036	1165.1	0.89223	679.52
0.08368	528.20	0.37992	1240.0	0.92505	511.87
0.10501	628.96	0.52757	1293.6	0.95133	356.97
0.12540	715.55	0.60909	1280.4	0.96898	235.98
0.16339	851.42	0.69156	1216.9	0.99382	49.39
0.21931	1004.0	0.78368	1051.7		

Table 1 (*Continued*)

x	H^{E}/(J mol^{-1})	x	H^{E}/(J mol^{-1})	x	H^{E}/(J mol^{-1})
(1 − x)n-Pentylbenzene + xMMTSO					
0.02145	179.76	0.30022	902.78	0.69582	810.42
0.04768	358.88	0.31714	912.50	0.72714	797.92
0.10921	650.68	0.36145	889.25	0.74406	803.47
0.13031	763.89	0.43953	893.75	0.82469	768.75
0.15407	838.19	0.52310	867.02	0.89021	657.64
0.17567	898.61	0.60475	847.22	0.91397	569.44
0.24306	899.38	0.62209	830.32	0.93673	405.93
0.26099	899.90	0.64466	823.38	0.95398	329.40
0.29326	920.43	0.66955	819.44	0.96906	271.21
(1 − x)n-Hexylbenzene + xMMTSO					
0.01819	135.22	0.19393	817.85	0.77384	571.50
0.02268	189.85	0.29420	766.80	0.78373	566.59
0.05303	384.98	0.29625	787.77	0.81450	557.51
0.05908	418.33	0.38309	768.89	0.82673	544.19
0.07532	495.86	0.42778	739.83	0.86833	525.38
0.10497	623.49	0.43701	731.42	0.90623	453.53
0.11342	627.15	0.53499	698.55	0.93687	360.45
0.14798	742.74	0.62728	644.49	0.94385	327.37
0.12943	690.07	0.66219	624.80	0.97202	185.79
0.17875	808.72	0.72631	606.97		
(1 − x)n-Heptylbenzene + xDMSO					
0.02644	197.79	0.23877	657.98	0.90391	344.35
0.05257	356.22	0.41121	622.28	0.95638	293.57
0.08969	576.69	0.43142	618.43	0.97501	161.59
0.12627	645.19	0.59087	532.35	0.98708	34.96
0.15574	650.09	0.76478	447.79	0.99006	92.38
0.15966	660.16	0.85646	380.41		
0.21717	661.80	0.88343	360.68		
(1 − x)n-Octylbenzene + xDMSO					
0.02770	221.49	0.40624	498.94	0.96627	322.88
0.03569	273.26	0.54992	460.17	0.96981	265.84
0.04891	352.43	0.57218	452.54	0.97784	215.36
0.07087	485.16	0.69713	415.47	0.98550	135.26
0.16290	566.74	0.77858	381.57	0.98732	112.22
0.20337	552.97	0.88533	349.15	0.99213	75.64
0.33187	519.73	0.94047	332.20		

Figs. 1 and 2. All the excess enthalpies of alkylbenzene + MMTSO and alkylbenzene +DMSO observed were positive over the whole ranges of mole fractions at this temperature. *n*-Pentylbenzene, *n*-hexylbenzene, *n*-heptylbenzene and *n*-octylbenzene showed heterogeneous phase regions. Excess enthalpies of homogeneous mixtures for alkylbenzene + MMTSO and alkylbenzene +DMSO were fitted with Eq. (1) by the method of least squares. They are represented as solid lines in Figs. 1 and 2 with those of benzene and toluene + MMTSO and toluene +DMSO [2,6].

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

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

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

are given in Table 2.

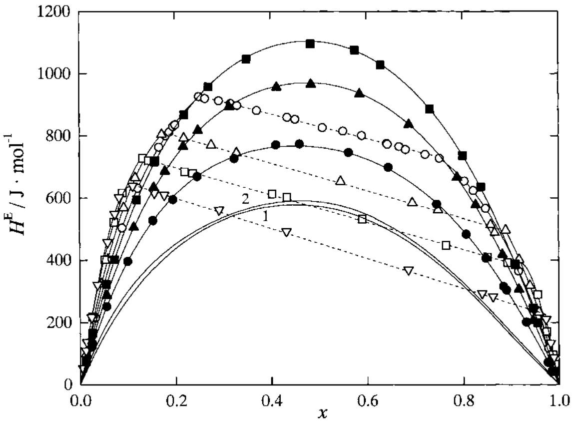

Fig. 1. Excess enthalpies of $(1-x)$ alkylbenzene + xMMTSO at 298.15 K: (●), ethylbenzene + MMTSO; (▲), *n*-propylbenzene + MMTSO; (■), *n*-butylbenzene + MMTSO; (○), *n*-pentylbenzene + MMTSO; (△), *n*-hexylbenzene + MMTSO; (□), *n*-heptylbenzene + MMTSO; (▽), *n*-octylbenzene + MMTSO. 1, Benzene + MMTSO[2]; and 2, toluene + MMTSO [6].

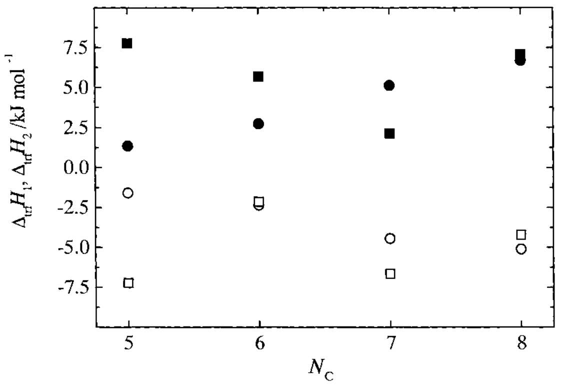

Fig. 2. Excess enthalpies of $(1-x)$ alkylbenzene + xDMSO at 298.15 K: (●), ethylbenzene + DMSO; (▲), *n*-propylbenzene + DMSO; (■), *n*-butylbenzene + DMSO; (○), *n*-pentylbenzene + DMSO; (△), *n*-hexylbenzene + DMSO; (□), *n*-heptylbenzene + DMSO; (▽), *n*-octylbenzene + DMSO. 1, Benzene + DMSO [2]; and 2, toluene + DMSO [15].

The excess enthalpies of alkylbenzenes from benzene to *n*-butylbenzene + MMSTO were increased with increasing size of alkyl groups of alkylbenzenes as the mixtures of *n*-alkane-1-ol + MMSTO [5] and *n*-alkane-1-nitril + MMTSO [13].

Excess enthalpies for heterogeneous mixtures were fitted with Eq. (3) and are given as broken lines in Figs. 1 and 2.

$$H^E = A_1 + A_2 x \tag{3}$$

The mixtures of alkylbenzenes + MMTSO were the second systems which had miscibility gaps in MMTSO among the previously observed 47 solvents [2–13]. The miscibility gap of *n*-octylbenzene + MMTSO was the largest among *n*-pentylbenzene, *n*-hexylbenzene, *n*-heptylbenzene and *n*-octylbenzene mixtures of MMTSO. The excess enthalpies of heterogeneous mixtures for *n*-octylbenzene + MMTSO was the least among other mixtures of alkylbenzene + MMTSO. The features for alkylbenzenes + DMSO were similar to those for the mixtures of MMTSO; however, enthalpic unstablizations on mixing were larger than those for the corresponding alkylbenzene mixtures with MMTSO except the homogeneous mixture of *n*-octylbenzene + DMSO in low mol fraction of 0.4 of DMSO.

The mutual solubilities $x(\mathrm{I})$ and $x(\mathrm{II})$ of alkylbenzene + MMTSO and alkylbenzene + DMSO at 298.15 K were determined from the coefficients of Eqs. (1) and (3), and are listed in Table 3. The miscibility gaps were increases with increasing size of alkyl radicals in alkylbenzenes. Excess enthalpies of 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 alkylbenzene-rich and sulfide-rich phases, respectively. Observed heats of mixing, q, of 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 means the total amounts of the alkylbenzene and the sulfide in a mixture and $x(\mathrm{I})$ and $x(\mathrm{II})$ the mutual solubilities of the sulfides in the mixture [8]. This Eq. (4) may be rearranged as

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

Comparing Eq. (5) with Eq. (3), $H^E(\mathrm{I})$ and $H^E(\mathrm{II})$ were determined, where

$$H^E(\mathrm{I}) = H^E, \quad \text{when } x = x(\mathrm{I}), \tag{6}$$

Table 2
Best-fit values for the coefficients A_i of Eqs. (1) and (3) with the calculated standard deviations of the fit s_f

System	Equation	A_1	A_2	A_3	A_4	s_f/(J mol^{-1})
$(1-x)$Ethylbenzene + xMMTSO	Eq. (1)	3052.5	356.7	1130.2	646.4	3.7
$(1-x)n$-Propylbenzene + xMMTSO	Eq. (1)	3874.8	2553.0	1118.1	633.5	2.9
$(1-x)n$-Butylbenzene + xMMTSO	Eq. (1)	4409.5	267.0	1313.4	548.2	4.0
$(1-x)n$-Pentylbenzene + xMMTSO						
$x < 0.25$, $0.76 < x$	Eq. (1)	3909.0	1019.3	2462.6		2.8
$0.25 < x < 0.76$	Eq. (3)	1027.9	−394.8			3.0
$(1-x)n$-Hexylbenzene + xMMTSO						
$x < 0.24$, $0.75 < x$	Eq. (1)	3478.0	885.5	3824.1		2.7
$0.24 < x < 0.75$	Eq. (3)	885.7	−433.9			3.9
$(1-x)n$-Heptylbenzene + xMMTSO						
$x < 0.13$, $0.95 < x$	Eq. (1)	4495.0	709.3	3682.0		2.8
$0.13 < x < 0.95$	Eq. (3)	786.5	−439.8			5.5
$(1-x)n$-Octylbenzene + xMMTSO						
$x < 0.13$, $0.95 < x$	Eq. (1)	4112.6	557.4	4822.6		1.5
$0.13 < x < 0.95$	Eq. (3)	694.1	−475.8			4.5
$(1-x)$Ethylbenzene + xDMSO	Eq. (1)	4034.0	−66.2	1308.5	48.5	3.8
$(1-x)n$-Propylbenzene + xDMSO	Eq. (1)	4800.0	−51.5	1914.3	50.1	2.5
$(1-x)n$-Butylbenzene + xDMSO	Eq. (1)	5167.5	−325.5	2774.6	108.3	1.9
$(1-x)n$-Pentylbenzene + xDMSO						
$x < 0.19$, $0.86 < x$	Eq. (1)	9866.6	−170.5	−1362.6		4.1
$0.19 < x < 0.86$	Eq. (3)	1022.3	−307.2			3.4
$(1-x)n$-Hexylbenzene + xDMSO						
$x < 0.14$, $0.91 < x$	Eq. (1)	3896.5	−440.2	5145.3		4.0
$0.14 < x < 0.91$	Eq. (3)	951.8	−505.1			3.9
$(1-x)n$-Heptylbenzene + xDMSO						
$x < 0.15$, $0.96 < x$	Eq. (1)	7963.1	−382.4	1485.8		2.2
$0.15 < x < 0.96$	Eq. (3)	810.0	−483.4			5.0
$(1-x)n$-Octylbenzene + xDMSO						
$x < 0.15$, $0.96 < x$	Eq. (1)	3214.9	−472.9	6039.2		3.9
$0.15 < x < 0.96$	Eq. (3)	620.2	−303.3			4.9

Table 3
Mutual solubilities, x(I) and x(II), and excess enthalpies at saturation of $(1-x)\{n\text{-}CH_3(CH_2)_iC_6H_5, i = 4{\sim}7\} + x$MMTSO and $(1-x)\{n\text{-}CH_3(CH_2)_iC_6H_5, i = 4{\sim}7\} + x$DMSO at 298.15 K

System	x(I)	x(II)	H^E(I)/(J mol^{-1})	H^E(II)/(J mol^{-1})
$(1-x)n$-Pentylbenzene + xMMTSO	0.2412	0.7684	932.7	724.5
$(1-x)n$-Hexylbenzene + xMMTSO	0.1714	0.8905	811.3	499.3
$(1-x)n$-Heptylbenzene + xMMTSO	0.1151	0.9413	735.9	372.5
$(1-x)n$-Octylbenzene + xMMTSO	0.0921	0.9694	650.3	232.9
$(1-x)n$-Pentylbenzene + xDMSO	0.1253	0.9102	983.8	742.7
$(1-x)n$-Hexylbenzene + xDMSO	0.1871	0.9381	897.3	478.0
$(1-x)n$-Heptylbenzene + xDMSO	0.0981	0.9627	762.6	344.7
$(1-x)n$-Octylbenzene + xDMSO	0.0967	0.9611	590.9	328.7

and

$$H^E(\mathrm{II}) = H^E \quad \text{when } x = x(\mathrm{II}) \tag{7}$$

The values of H^E(I) and H^E(II) are listed in Table 3 and are plotted in Fig. 3. Both, the excess enthalpies of alkylbenzene-rich mixtures, H^E(I), and those of

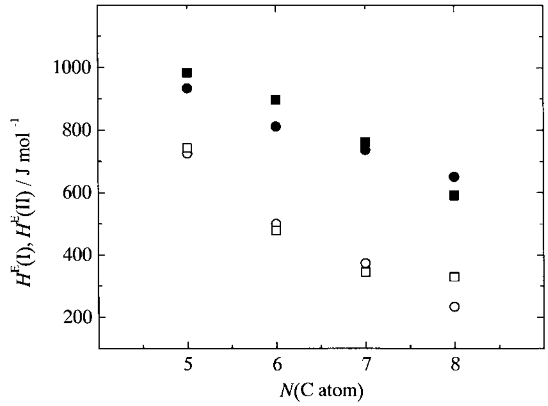

Fig. 3. Excess enthalpies of alkylbenzene-rich mixtures (mixture I), and those of sulfide-rich mixtures (mixture II) at 298.15 K in liquid–liquid equilibria. Circles and squares refer to the mixtures of MMTSO and DMSO, respectively. Filled, mixture I; open, mixture II.

sulfoxide-rich ones, H^E(II), decreased in the numbers of carbon atoms in alkylbenzene molecules. This may be the result of the competition among (1) the decrease in numbers of strong dipolar contacts between sulfides, (2) the decrease in numbers of weak electro-quadrapolar interaction between alkylbenzene molecules, and (3) the formation of new dipole-induced dipole attractions between the phenyl groups and the sulfoxides, and the decreasing tendency of mutual solubilities with an increase in the numbers of carbon-atoms in the alkyl groups of alkylbenzenes. Fig. 3 clearly tells us that there is a decrease in the relative number of unfavorable contacts between unlike molecules with an increase in N (i.e., increase in the length of alkyl radicals in alkylbenzenes), corresponding to the decrease in mutual solubility.

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

As the change in partial molar Gibbs energy between conjugate mixtures is zero, 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 alkylbenzenes were endothermic, accompanying the increase in partial molar entropy, and those of the sulfoxides were exothermic, accompanying the decrease in partial molar entropies. This shows that the strong dipolar interaction may hinder the molecular motions in mixtures. Therefore, the large decrease in enthalpic stabilization of dipole–dipole interactions on dilution with non-polar surfaces of alkylbenzenes and increase in entropy may occur due to increase in molecular rotations. The partial molar enthalpies of transfer of alkylbenzene (from n-pentylbenzene to n-octylbenzene) and those of MMTSO and DMSO showed linear relation as in Fig. 4, except for octylbenzene in DMSO and DMSO in hexylbenzene.

In order to consider pair interactions between alkylbenzenes and sulfoxides, excess partial molar enthalpies at infinite dilutions were determined from Eq. (1) with the coefficients in Table 2, and summarized in Table 6. The limiting excess partial molar enthalpies

Table 4
Partial molar excess enthalpies of conjugate mixtures of alkylbenzene + MMTSO or alkylbenzene +DMSO at 298.15 K

System	H_1^E(I)/kJ mol^{-1}	H_2^E(I)/kJ mol^{-1}	H_1^E(II)/(kJ mol^{-1})	H_2^E(II)/(kJ mol^{-1})
$(1-x)n$-Pentylbenzene $+ x$MMTSO	0.611	1.94	1.96	0.352
$(1-x)n$-Hexylbenzene $+ x$MMTSO	0.456	2.53	3.18	0.170
$(1-x)n$-Heptylbenzene $+ x$MMTSO	0.245	4.51	5.37	0.0609
$(1-x)n$-Octylbenzene $+ x$MMTSO	0.196	5.13	6.88	0.0228
$(1-x)n$-Pentylbenzene $+ x$DMSO	0.0802	7.29	7.84	0.0429
$(1-x)n$-Hexylbenzene $+ x$DMSO	0.539	2.24	6.21	0.0995
$(1-x)n$-Heptylbenzene $+ x$DMSO	0.0504	6.66	2.18	0.0218
$(1-x)n$-Octylbenzene $+ x$DMSO	0.220	4.28	7.28	0.0453

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

System	$\Delta_{trf}H_1$/(kJ mol$^{-)1}$	$\Delta_{trf}H_2$/(kJ mol^{-1})	$\Delta_{trf}H_1$/(JK^{-1} mol^{-1})	$\Delta_{trf}H_2$/(JK^{-1} mol^{-1})
$(1-x)n$-Pentylbenzene + xMMTSO	1.35	−1.59	4.52	−5.34
$(1-x)n$-Hexylbenzene + xMMTSO	2.72	−2.36	9.12	−7.91
$(1-x)n$-Heptylbenzene + xMMTSO	5.12	−4.44	17.2	−14.9
$(1-x)n$-Octylbenzene + xMMTSO	6.68	−5.11	22.4	−17.1
$(1-x)n$-Pentylbenzene + xDMSO	7.76	−7.25	26.0	−24.3
$(1-x)n$-Hexylbenzene + xDMSO	5.68	−2.14	19.0	−7.18
$(1-x)n$-Heptylbenzene + xDMSO	2.13	−6.67	7.15	−22.4
$(1-x)n$-Octylbenzene + xDMSO	7.06	−4.22	23.7	−14.2

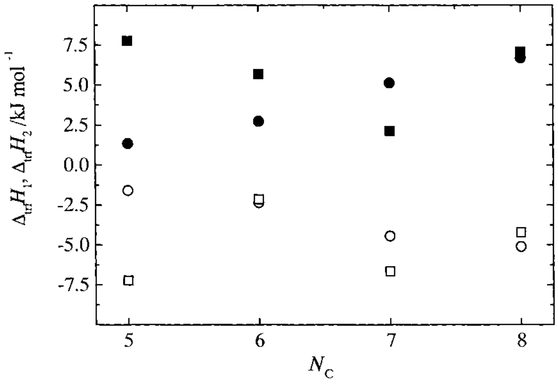

Fig. 4. Correlation between enthalpies of transfer and number of carbon atoms for the alkyl radicals in alkylbenzens. Circles and squares refer to the mixtures of MMTSO and DMSO, respectively. Filled and open circles denote those for the 1 and 2, respectively.

of alkylbenzene + MMTSO and alkylbenzene + DMSO were seen to increase with increasing size of alkyl groups, as shown in Fig. 5. The limiting excess partial molar enthalpies of the alkylbenzenes, $H_1^{E,\infty}$, of all the mixtures with MMTSO studied, were smaller than those of MMTSO. For the mixtures with DMSO, the same is also obtained for benzene, toluene and ethylbenzene. However, $H_1^{E,\infty} > H_2^{E,\infty}$, when alkyl radicals are longer than n-propyl. The similar results were obtained for the mixtures of methyl benzenes, and cycloethers + MMTSO [6,7], although the mixtures of MMTSO with water [2], and chloromethanes [3,4] were different. $H_1^{E,\infty}$ and $H_2^{E,\infty}$ of alkylbenzene(n-hexylbenzene to n-octylbenzene) + DMSO were almost constant as those of the mixtures of n-alkane-ol + DMSO [15].

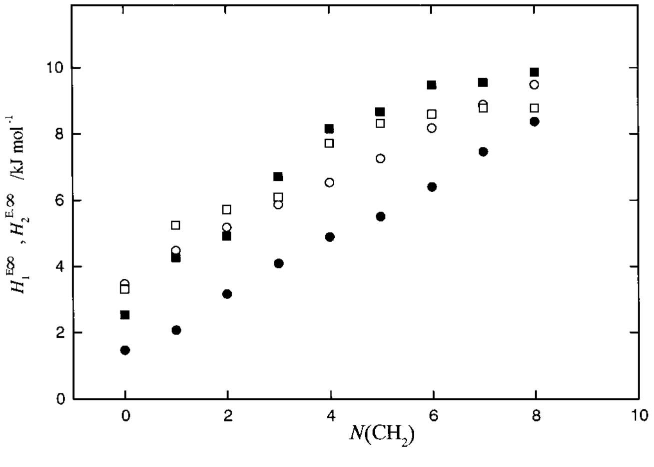

Fig. 5. Limiting partial molar enthalpies of alkylbenzenes(1) + sulfoxide(2) at 298.15 K; circles, alkylbenzene + MMTSO; squares, alkylbenzene + DMSO. Open symbol, alkylbenzene; and solid symbol, sulfoxide.

Table 6
Excess partial molar enthalpies at infinite dilution at 298.15 K

System	$H_1^{\mathrm{E},\infty}$/(kJ mol^{-1})	$H_2^{\mathrm{E},\infty}$/(kJ mol^{-1})
Ethylbenzene(1) + MMTSO(2)	3.17	5.19
n-Propylbenzene(1) + MMTSO(2)	4.10	5.88
n-Butylbenzene(1) + MMTSO(2)	4.90	6.54
n-Pentylbenzene(1) + MMTSO(2)	5.52	7.27
n-Hexylbenzene(1) + MMTSO(2)	6.41	8.18
n-Heptylbenzene(1) + MMTSO(2)	7.47	8.89
n-Octylbenzene(1) + MMTSO(2)	8.38	9.49
Ethylbenzene(1) + DMSO(2)	4.92	5.73
n-Propylbenzene(1) + DMSO(2)	6.27	6.71
n-Butylbenzene(1) + DMSO(2)	8.16	7.72
n-Pentylbenzene(1) + DMSO(2)	8.67	8.33
n-Hexylbenzene(1) + DMSO(2)	9.48	8.60
n-Heptylbenzene(1) + DMSO(2)	9.55	8.79
n-Octylbenzene(1) + DMSO(2)	9.86	8.78
Benzene(1) + MMTSO(2) [a]	1.48	3.48
Toluene(1) + MMTSO(2) [b]	2.08	4.49
Benzene(1) + DMSO(2) [a]	2.54	3.32
Toluene(1) + DMSO(2) [c]	4.27	5.25

[a] Cited from [2].
[b] Cited from [6].
[c] Cited from [15].

Although the effect of breaking the dipole–dipole stabilization between sulfoxide molecules by addition of alkylbenzenes are important, it may be worthwhile to calculate the effects of dipole-induced dipole interaction between sulfoxide and the aromatic molecules used here.

A dipole-induced dipole interaction energy u_{12} can be expressed as [16]:

$$u_{12} = -\frac{\alpha_2\mu_1^2 + \alpha_1\mu_2^2}{r^6} \tag{8}$$

Thus, the interaction energy due to dipole-induced dipole interaction might be proportional to $(\alpha_2\mu_1^2 + \alpha_1\mu_2^2)V_1^{-1}V_2^{-1}$, where α, μ and V are the polarizability, the dipole moment and the molar volume of pure component, respectively. Linear relationships were obtained, as shown in Fig. 6, between the limiting excess partial molar enthalpies of the mixtures of alkylbenzenes + MMTSO and alkylbenzenes +DMSO and sum of the products of polarizability and square of the dipole moment divided by the products of molar volumes of pure components. The constants and coefficients of Eq. (9) and the standard deviations are listed in Table 7.

$$H^{\mathrm{E},\infty} = a + b(\alpha_2\mu_1^2 + \alpha_1\mu_2^2)V_1^{-1}V_2^{-1} \tag{9}$$

The values of enthalpic stabilization of alkylbenzene + MMTSO or alkylbenzene +DMSO and dipole-induced dipole interaction energies show a good linearity for the observed mixtures of

Table 7
Best fit for the coefficients of Eq. (9)

System	$H_1^{\mathrm{E},\infty}$/(kJ mol^{-1})	a	$10^{62}b$	s_f/(J mol^{-1})
n-Alkylbenzene + MMTSO	$H_1^{\mathrm{E},\infty}$	0.772	0.852	0.24
	$H_2^{\mathrm{E},\infty}$	0.09	0.901	0.07
n-Alkylbenzene + DMSO	$H_1^{\mathrm{E},\infty}$	0.401	1.69	0.18
	$H_2^{\mathrm{E},\infty}$	1.44	1.34	0.49

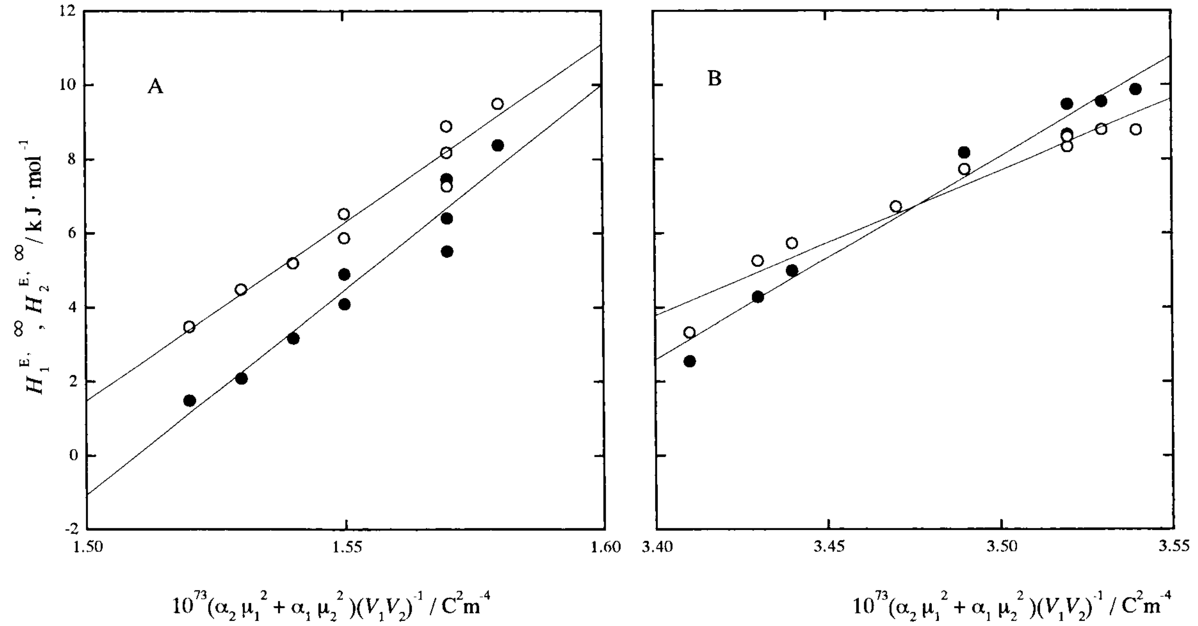

Fig. 6. Correlation between the limiting partial molar excess enthalpies and $(\alpha_2\mu_1^2+\alpha_1\mu_2^2)V_1^{-1}V_2^{-1}$ from benzene to *n*-octylbenzene. A, the mixtures of alkylbenzenes(1) + MMTSO(2); and B, those of alkylbenzenes (1) + DMSO(2). Open and filled symbols show $H_1^{E,\infty}$ and $H_2^{E,\infty}$, respectively.

alkylbenzene + MMTSO or alkylbenzene +DMSO. The dipole moment of DMSO(dipole moment: 13.4×10^{-30} Cm) [17] is larger than that of MMTSO molecules (10.7×10^{-30} Cm) [15] in the pure liquid state. The mixtures containing DMSO may absorb larger heats than those containing MMTSO, owing to the insertion of non-polar molecules of the alkylbenzenes.

It was explained that the major effect on the excess enthalpies of alkylbenzenes + MMTOS or alkylbenzenes + DMSO might arise from hindering of stable dipolar stabilization by the less or non-polar components of alkylbenzenes and increase in the stabilization by the dipole-induced dipole interactions between the sulfoxide molecules and alkylbenzene molecules.

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