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

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Excess enthalpies of sixteen binary mixtures between one each of methyl methylthiomethyl sulfoxide (MMTSO) and dimethyl sulfoxide (DMSO) and one of ketone $\{CH_3CO(CH_2)_nCH_3$, $n=0$ to 6 and $CH_3COC_6H_5\}$ have been determined at 298.15 K. All the mixtures showed positive excess enthalpies over the whole range of mole fractions. Excess enthalpies of ketone+MMTSO or DMSO increased with increasing the number of methylene radicals in the methyl alkyl ketone molecules. Excess enthalpies of MMTSO+ketone are smaller than those of DMSO+ketone for the same ketone mixtures. The limiting excess partial molar enthalpies of the ketone, $H_1^{E,\infty}$, in all the mixtures with MMTSO were smaller than those of DMSO. Linear relationships were obtained between limiting excess partial molar enthalpies and the number of methylene groups except 2-propanone.

Keywords: acetophenone, 2-alkanones, CH$_3$CO(CH$_2$)$_n$CH$_3$, dimethyl sulfoxide, excess enthalpy, methyl methylthiomethyl sulfoxide

Introduction

In our previous papers, excess thermodynamic functions for the binary mixtures of methyl methyl-thiomethyl sulfoxide (MMTSO) and water, benzene, dimethyl sulfoxide (DMSO) [1, 2], carbon tetrachloride, chloroform, dichloromethane [3], deutero-chloroform [4], aliphatic alcohol $\{CH_3(CH_2)_nOH$, $n=0$ to 12$\}$ [5, 6], six methylbenzenes $\{C_6H_{6-n}(CH_3)_n$, $n=1$ to 3$\}$ [7], five cycloethers [8], three aliphatic ethers [9], five monohalogenated aromatic compounds (benzene and toluene) [10], three aliphatic ethers [11], six *o*- and *m*-dihalogenated benzenes [12], aliphatic benzene [13], aliphatic amine [14], some nitriles $\{[CH_3(CH_2)_nCN$, $n=0$ to 12], benzonitrile$\}$ [15–18], and those of DMSO were reported.

To find the effect of the polar group in aliphatic compounds on the thermodynamic properties of mixtures, excess enthalpies of the mixtures between MMTSO and eight ketones of $\{CH_3CO(CH_2)_nCH_3$, $n=0$ to 6 and $CH_3COC_6H_5\}$ were determined over the whole range of mole fractions. The results are compared with those of previous aliphatic compounds to clarify the correlation between the thermodynamic properties of the mixtures and the molecular structures of their components. Those of aliphatic ketones+DMSO were also determined as the reference systems.

Experimental

Materials

Procedures for purification and the final purities of MMTSO (Nippon Soda Co.) and DMSO (Merck, uvasol) were the same as those described previously [1, 2]. Ketones of $\{CH_3CO(CH_2)_nCH_3$, $n=0$ to 6 and $CH_3COC_6H_5\}$ (Kishida Chemical) were fractionally distilled through a 1 m column over freshly activated molecular sieves 3A or 4A under ambient to 1 kPa. Molecular sieves had been evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa for activation. 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 on Yanagimoto G180FP showed merely 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 as 0.01 mol% or less.

Apparatus and procedures

A twin microcalorimeter of the 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 fractions. Details of the calorimetric procedures and reproducibility test of this calorimeter system are described elsewhere [2, 4, 10, 17, 19].

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Results and discussion

The experimental results of excess enthalpies are summarized in Table 1 and shown in Figs 1 and 2. The excess enthalpies of 2-alkanone+MMTSO or +DMSO are increased with increasing size of alkyl group. They were fitted with Eq. (1) using the method of least squares.

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

Coefficients A_i in Eq. (1) and standard deviations of fits s_f:

$$s_f = \left[\sum_{i=1}^{n} \{H^E(\text{expt}) - H^E(\text{calc})\}_i^2 /(n-k) \right]^{1/2} \qquad (2)$$
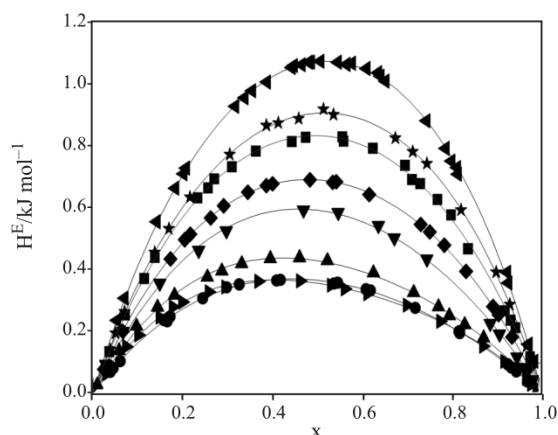
are given in Table 2.

Fig. 1 Excess enthalpies of $(1-x)CH_3(CH_2)_nCOCH_3$ (n=0–6)+xMMTSO at 298.15 K: ● – 2-propanone, ▲ – 2-butanone, ▼ – 2-pentanone, ◆ – 2-hexanone, ■ – 2-heptanone, ★ – 2-octanone, ◄ – 2-nonanone, ► – acetophenone
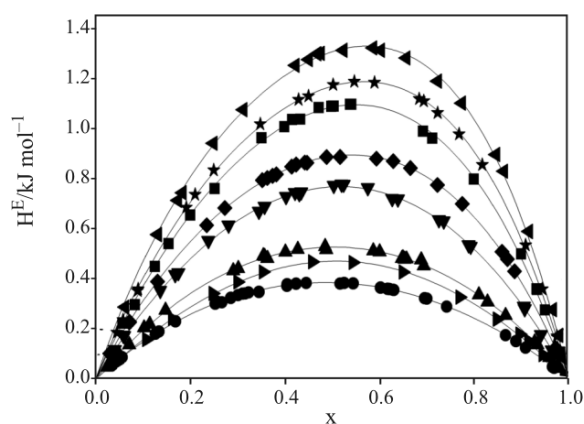
Fig. 2 Excess enthalpies of $(1-x)CH_3(CH_2)_nCOCH_3$ (n=0–6)+xDMSO at 298.15 K: ● – 2-propanone, ▲ – 2-butanone, ▼ – 2-pentanone, ◆ – 2-hexanone, ■ – 2-heptanone, ★ – 2-octanone, ◄ – 2-nonanone, ► – acetophenone

All the excess enthalpies observed are positive over the whole range of mole fractions at this temperature. The reported excess enthalpies of acetophenone +DMSO and 2-propanone+DMSO at 298.15 K by Clever and Pigott [20] are also plotted in Fig. 3. Those results of Clever and Pigott were 15 and 2% smaller than our results, respectively. Their isoperibol calorimeter has some vapor phase correction problems.
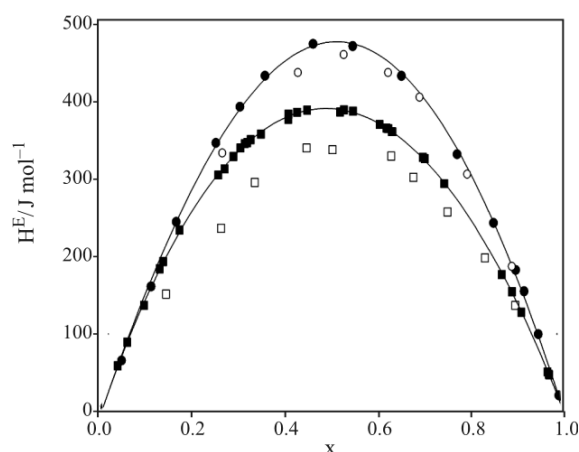

Fig. 3 Excess enthalpies of mixing at 298.15 K: circle – $(1-x)$acetophenone+xDMSO, square – $(1-x)$2-propanone+xDMSO, solid sign – this work, open sign – Clever *et al.* [20]: Solid lines show smoothed curve by Redlich–Kister type equation

Excess enthalpies of acetophenone+MMTSO or +DMSO were positive over the whole concentration range. Excess enthalpies of benzene+MMTSO and +DMSO [2] were also positive and 572, 588 J mol^{-1} at equimolar mixture, respectively. When CH_3CO radicals were substituted for hydrogen in benzene molecules, that is, acetophenone molecules, enthalpic destabilization of the systems was decreased by about 221 and 136 J mol^{-1}, respectively. The decreasing enthalpic destabilization of acetophenone+DMSO was smaller than that of acetophenone+MMTSO. The replacement of the polar group for counter components brought about a reduction in enthalpic destabilization.

As shown in Fig. 4, excess enthalpies of 2-propanone+MMTSO or +DMSO were positive over the whole concentration range. When methyl radical was substituted by phenyl radicals in 2-propanone molecules, that is, acetophenone molecules, the enthalpic destabilization of the mixtures was decreased by about 10 J mol^{-1} for the mixture of acetophenone+MMTSO, but was increased by about 86 J mol^{-1} for the mixture of acetophenone+DMSO at each equimolar mixture. Dipole–dipole interaction of the strong polar molecules of DMSO might be disturbed by the phenyl group. Furthermore, volume contraction of those systems may encourage the decrease in the enthalpic destabilization of those mixtures [21].

Table 1 Excess enthalpies of $(1-x)$ aliphatic ketones+x sulfoxides at 298.15 K

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
		$(1-x)$2-propanone+xMMTSO			
0.03667	71.26	0.2975	343.3	0.7172	277.1
0.03896	71.08	0.3255	352.9	0.8143	201.0
0.04573	83.31	0.4086	365.5	0.8162	196.2
0.06150	105.4	0.4171	367.9	0.8163	202.4
0.1581	238.1	0.5364	355.7	0.9227	95.53
0.1655	234.1	0.5447	358.6	0.9305	85.81
0.1718	249.4	0.6078	337.5	0.9417	72.20
0.2441	308.1	0.6175	333.9	0.9665	40.41
		$(1-x)$2-butanone+xMMTSO			
0.009744	28.89	0.2867	396.2	0.7136	327.3
0.03378	85.38	0.3310	419.8	0.7689	280.7
0.05838	139.3	0.3947	436.3	0.7931	252.2
0.09715	218.5	0.4598	438.5	0.8272	223.2
0.1437	279.6	0.5217	429.9	0.8688	180.4
0.1816	318.5	0.6241	390.2	0.9445	83.30
0.2546	376.8	0.7136	327.3	0.9683	48.66
		$(1-x)$2-pentanone+xMMTSO			
0.02885	85.64	0.4686	592.1	0.8835	227.2
0.06759	183.5	0.5456	584.6	0.9043	193.0
0.1486	357.2	0.6354	532.3	0.9431	119.0
0.2353	462.8	0.6706	502.8	0.9598	85.30
0.2968	525.2	0.7430	435.0	0.9786	45.91
		$(1-x)$2-hexanone+xMMTSO			
0.02464	79.40	0.3860	671.2	0.7818	479.3
0.06675	202.1	0.3999	677.1	0.8300	395.5
0.1722	435.3	0.4830	689.9	0.8899	282.0
0.2041	496.7	0.5336	681.9	0.9022	255.7
0.2167	514.5	0.5415	683.4	0.9323	183.8
0.2620	567.2	0.6146	642.4	0.9707	85.85
0.2910	606.0	0.7292	545.8		
0.3446	650.0	0.7496	521.7		
		$(1-x)$2-heptanone+xMMTSO			
0.3649	135.7	0.3624	782.1	0.7284	677.1
0.07217	254.4	0.4424	812.7	0.7666	626.0
0.1143	371.7	0.4734	826.6	0.7970	576.4
0.1380	439.5	0.5549	827.8	0.8344	467.3
0.2328	631.1	0.5579	813.9	0.9163	267.6
0.2560	663.4	0.6229	791.0	0.9289	237.6
0.2699	692.3	0.6947	715.9	0.9398	213.6
0.3091	731.3	0.7100	689.9	0.9725	118.7
		$(1-x)$2-octanone+xMMTSO			
0.03851	143.1	0.3860	865.3	0.7431	742.1
0.05069	196.1	0.4123	873.1	0.8190	592.7
0.0707	265.2	0.4577	886.9	0.8969	392.8
0.1375	456.1	0.53131	917.9	0.9272	288.5
0.1688	532.2	0.5353	899.9	0.9644	154.1
0.2158	633.5	0.6729	824.5	0.9755	101.8
0.3043	771.7	0.7116	780.4		
		$(1-x)$2-nonanone+xMMTSO			
0.05341	237.1	0.4469	1058	0.6508	1008
0.07038	309.0	0.4642	1061	0.7422	879.9
0.1418	554.7	0.4800	1069	0.7849	791.2
0.1829	662.6	0.4852	1069	0.7946	750.2
0.2013	709.1	0.5059	1072	0.8102	729.2
0.2069	727.8	0.5445	1069	0.8117	707.8
0.3165	926.2	0.5643	1062	0.9213	392.6
0.3370	954.0	0.5761	1066	0.9239	358.2
0.3538	977.0	0.6089	1049	0.9691	160.8
0.3870	1005	0.6344	1035	0.9814	105.6
0.4423	1052	0.6398	1024		

Table 1 Continued

x	$H^E/$J mol^{-1}	x	$H^E/$J mol^{-1}	x	$H^E/$J mol^{-1}
		$(1-x)$2-acetophenone$+x$MMTSO			
0.02990	65.23	0.2945	345.0	0.8677	153.8
0.04271	90.84	0.3680	363.4	0.9149	104.9
0.07397	153.0	0.4608	364.5	0.9632	49.93
0.1011	190.1	0.5295	350.3	0.9745	31.14
0.1483	247.9	0.5601	339.2	0.9864	17.05
0.1775	280.6	0.6106	323.7	0.9863	12.33
0.1987	296.5	0.6985	286.5		
0.2576	329.1	0.7727	234.3		
		$(1-x)$2-propanone$+x$DMSO			
0.03584	58.95	0.3231	347.3	0.6283	357.8
0.05621	89.181	0.3453	349.5	0.6300	357.4
0.1263	182.9	0.4044	373.5	0.6955	324.9
0.1339	192.1	0.4049	379.9	0.6997	323.1
0.1686	232.3	0.4236	382.4	0.7417	291.4
0.2526	302.3	0.4450	385.1	0.8659	176.9
0.2562	310.5	0.5165	382.6	0.8878	153.7
0.2668	308.5	0.5250	385.2	0.9081	127.4
0.2855	325.8	0.5444	383.7	0.9650	51.36
0.3008	336.9	0.6019	366.7	0.9676	48.25
0.3103	342.4	0.6168	362.1	0.9686	47.42
0.3157	343.5	0.6206	361.3		
		$(1-x)$2-butanone$+x$DMSO			
0.02535	50.14	0.3630	482.7	0.6878	477.1
0.03276	67.27	0.4009	508.3	0.6934	453.5
0.04996	101.6	0.4271	519.1	0.8099	337.9
0.07138	139.4	0.4849	530.4	0.8281	309.9
0.1028	206.4	0.4875	518.6	0.8660	255.6
0.1142	220.6	0.5868	513.3	0.9272	149.9
0.1476	276.4	0.6001	509.5	0.9330	139.5
0.2908	433.5	0.6472	483.3	0.9585	88.13
0.3014	442.8	0.6493	486.0	0.9758	53.49
0.3543	493.2	0.6527	480.1	0.9794	44.87
0.3572	490.9	0.6569	481.1		
		$(1-x)$2-pentanone$+x$DMSO			
0.04104	119.5	0.4022	728.9	0.7252	636.4
0.05891	177.2	0.4213	744.5	0.7356	630.9
0.06067	175.2	0.4301	740.1	0.7881	537.0
0.1363	355.4	0.4343	746.6	0.7924	531.1
0.1682	418.4	0.5030	773.2	0.9049	292.0
0.1749	426.1	0.5196	777.9	0.9064	282.4
0.2380	553.8	0.5242	777.5	0.9408	179.2
0.2808	614.8	0.5751	763.8	0.9640	118.0
0.3450	669.3	0.6266	720.3	0.9681	103.7
0.3570	689.4	0.6387	719.1		
		$(1-x)$2-hexanone$+x$DMSO			
0.03031	104.1	0.3820	817.4	0.7066	781.9
0.07159	228.1	0.4141	848.4	0.8059	610.1
0.07204	230.3	0.4236	856.6	0.8833	416.1
0.1307	390.5	0.4419	864.1	0.8958	375.2
0.2346	614.8	0.4879	886.2	0.9295	263.5
0.2729	683.1	0.5165	886.9	0.9457	209.5
0.3522	794.3	0.5432	885.5	0.9786	87.97
0.3627	802.8	0.6393	841.3		
0.3737	811.4	0.6395	847.6		

Table 1 Continued

x	$H^E/J\ mol^{-1}$	x	$H^E/J\ mol^{-1}$	x	$H^E/J\ mol^{-1}$
		$(1-x)$2-heptanone$+x$DMSO			
0.05685	224.3	0.4325	1037	0.7991	799.6
0.08337	305.5	0.4715	1073	0.8988	490.4
0.1253	450.8	0.4978	1088	0.9311	361.7
0.1541	541.8	0.5018	1089	0.9321	349.4
0.1997	654.9	0.5029	1089	0.9488	277.7
0.2515	769.1	0.5376	1096	0.9818	109.3
0.3507	952.3	0.5405	1096	0.9827	100.5
0.3987	1007	0.6921	988.7		
0.4152	1035	0.7113	981.0		
		$(1-x)$2-octanone$+x$DMSO			
0.04521	192.7	0.4289	1115	0.7679	982.2
0.05813	243.3	0.4497	1129	0.8171	855.3
0.08869	358.9	0.5019	1175	0.9081	521.4
0.09020	360.5	0.5466	1187	0.9433	350.7
0.1916	685.4	0.5891	1183	0.9745	163.4
0.2103	736.9	0.6837	1118	0.9860	101.3
0.2496	834.0	0.6936	1109		
0.3478	1017	0.7228	1068		
		$(1-x)$2-nonanone$+x$DMSO			
0.03854	197.2	0.4503	1271	0.7227	1209
0.07105	349.1	0.4682	1288	0.7735	1101
0.1043	484.6	0.4753	1290	0.8455	885.6
0.1569	672.2	0.5232	1311	0.8622	818.7
0.1836	759.1	0.5859	1321	0.9149	565.2
0.2486	935.3	0.6024	1321	0.9657	258.8
0.3117	1072	0.6176	1318	0.9788	160.6
0.4218	1242	0.6563	1291	0.9906	72.64
		$(1-x)$2-acetophenone$+x$DMSO			
0.04399	66.00	0.3535	429.1	0.8477	241.3
0.1073	160.4	0.4576	469.6	0.8954	181.4
0.1617	242.6	0.5435	466.8	0.9138	154.3
0.2474	343.2	0.6491	428.9	0.9443	99.54
0.2997	389.5	0.7692	329.0	0.9892	21.47

Comparing excess enthalpies of the mixture containing MMTSO with that of DMSO for the same ketone, excess enthalpies of the mixtures containing DMSO are larger than those of MMTSO. This is similar to the behavior of polar substances in previous works. The mixtures containing MMTSO were less stable or more unstable than those of DMSO when the other component was polar, irrespective of whether aprotic or protic, namely water [2], chloroform, deuterochloroform [5], dichloromethane [4] and aliphatic alcohols [6]. However, the mixtures containing MMTSO were less unstable than those of DMSO when the other component was non-polar, such as benzene [2] and methylbenzene [7]. The major reason for these results might be the smaller decrease in stabilization of dipole-dipole interaction due to dilution by methyl and long non-polar alkyl groups because dipole-dipole stabilization of pure MMTSO ($\mu=10.7\cdot10^{-30}$ C m) [6] may be smaller than that of DMSO ($\mu=13.4\cdot10^{-30}$ C m) [22]. The calculated dipole moment of 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone and 2-nonanone
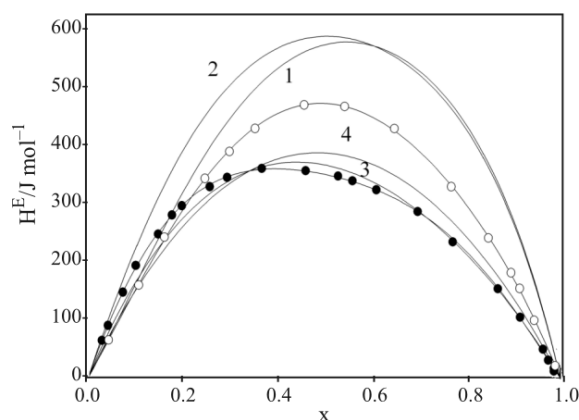
Fig. 4 Excess enthalpies of mixing at 298.15 K:
● – acetophenone+MMTSO, ○ – acetophenone+DMSO, 1– C$_6$H$_6$+MMTSO, 2 – C$_6$H$_6$+DMSO, 3 – 2-propanone+MMTSO, 4 – 2-propanone+DMSO

is 10.48, 10.04, 9.71, 9.89, 9.77, 9.75 and $9.62\cdot10^{-30}$ C m, respectively [23]. Even though these 2-alkanone might belong to dipolar molecules from the

point of view of the dipole moment, the behaviors of enthalpic results from this work were like non-dipolar molecules such as benzene [2], methylbenzenes [7] and cycloethers [8]. The dipole moment of 2-propanone is the largest in these 2-alkanones, which investigated in this work. Furthermore, the excess molar volumes of the systems measured were negative over the whole mole fraction range and increased with increasing size of alkyl radicals but were not proportional to the number of CH_2 radicals [21]. This might be one reason that destabilization on mixing does not simply increase with increasing CH_2 radicals in 2-alkanone.

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies at infinite dilutions were determined from Eq. (1) with the coefficients in Table 2, and are summarized in Table 3. The excess partial molar enthalpies at infinite dilution H_1^E are plotted *vs.* the number of methylene radicals for ketone in Fig. 5. A good correlation was obtained between the limiting excess partial molar enthalpies of ketone in MMTSO or DMSO and the number of methylene radicals of ketone except the systems including 2-propanone. These relationships can be written by:

$$H_1^E(\text{MMTSO})/\text{kJ mol}^{-1}=0.844+0.745n(\text{CH}_2)$$

$$s_f=0.071 \text{ kJ mol}^{-1}$$

$$H_2^E(\text{MMTSO})/\text{kJ mol}^{-1}=2.14+0.4531n(\text{CH}_2)$$

$$s_f=0.10 \text{ kJ mol}^{-1}$$

$$H_1^E(\text{DMSO})/\text{kJ mol}^{-1}=1.18+1.12n(\text{CH}_2)$$

$$s_f=0.040 \text{ kJ mol}^{-1}$$

$$H_2^E(\text{DMSO})/\text{kJ mol}^{-1}=1.66+0.624n(\text{CH}_2)$$

$$s_f=0.10 \text{ kJ mol}^{-1}$$

The CH_2 radical increments for enthalpic destabilization in 2-alkanone+MMTSO mixtures was 0.745 kJ mol^{-1} {(CH$_2$)}$^{-1}$, and those of cycloether and alkane-1-ol were 0.27 [8] and 1.0 kJ mol^{-1} {(CH$_2$)}-1 [6], respectively. On the other hand, the methyl radical increments for enthalpic destabilization of methyl benzenes+MMTSO mixtures were 0.67 kJ mol^{-1} {(CH$_2$)}$^{-1}$ [7]. The sequence of the CH_2 radical increments for enthalpic destabilization is as follows:

cycloether<methylbenzene<ketone<alkane-1-ol

All positive excess enthalpies of ketone+ MMTSO and +DMSO in the present investigation suggested that the effect of any weak hydrogen-bonded complex or any dipole–dipole interaction is smaller than that of each pure state. Because the positive excess enthalpies for the mixtures of

2-alkanone+MMTSO or +DMSO may mainly come from the breaking of strong self-interaction of dipole–dipole between each component of 2-alkanone and MMTSO or DMSO. The amphiphiles of ketones have two opposite interactions between sulfoxides. There might be significant dipole-dipole interaction effects on the limiting excess partial molar enthalpies of the mixtures between ketones and sulfoxides.

The dipole–dipole and dipole–induced dipole interaction energy of pair molecules [24] are shown as:

$$u_{12DD} = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{r^6 kT} \propto \frac{\mu_1^2\mu_2^2}{(r_1+r_2)^6} \qquad (3)$$

$$u_{12DI} = -\frac{\alpha_2\mu_1^2+\alpha_1\mu_2^2}{r^6} \propto \frac{\alpha_2\mu_1^2+\alpha_1\mu_2^2}{(r_1+r_2)^6} \qquad (4)$$

where u_{12DD}, u_{12DI}, α, μ, r and k are dipole–dipole interaction energy of pair molecules, dipole–induced dipole interaction energy of pair molecules, polarizability, dipole moment, distance between molecules, and Boltzmann constant, respectively. The molecular shapes of the components are not spherical, but as a first ap-
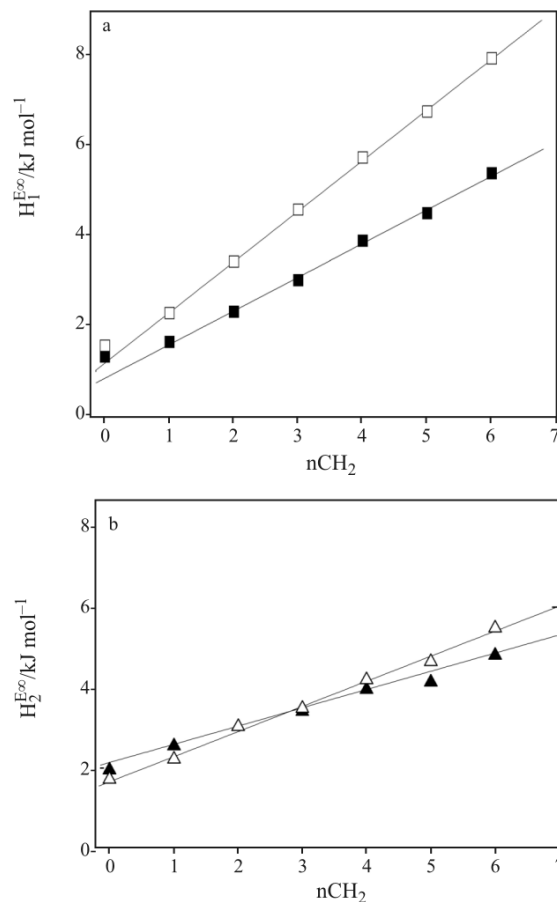

Fig. 5 Correlation between excess partial molar enthalpies at infinite dilution and number of methylene groups of aliphatic ketones nCH$_2$: a– partial molar enthalpies of ketones, b – partial molar enthalpies of sulfoxide: solid sign – MMTSO, open sign – DMSO

Table 2 Best-fit values for the coefficients A_i of Eq. (1) with the standard deviations of the fit s_f

Systems	A_1	A_2	A_3	s_f/J mol^{-1}
$(1-x)CH_3COCH_3+xMMTSO$	1467	314	167	3.1
$(1-x)CH_3CH_2COCH_3+xMMTSO$	1717	456	381	6.1
$(1-x)CH_3(CH_2)_2COCH_3+xMMTSO$	2367	358	302	7.0
$(1-x)CH_3(CH_2)_3COCH_3+xMMTSO$	2759	202	453	2.8
$(1-x)CH_3(CH_2)_4COCH_3+xMMTSO$	3328	60.1	553	4.7
$(1-x)CH_3(CH_2)_5COCH_3+xMMTSO$	3619	−178	693	5.4
$(1-x)CH_3(CH_2)_6COCH_3+xMMTSO$	4284	−271	805	5.4
$(1-x)C_6H_5COCH_3+xMMTSO$	1427	432	467	3.5
$(1-x)CH_3COCH_3+xDMSO$	1546	81.3	90.1	2.3
$(1-x)CH_3CH_2COCH_3+xDMSO$	2113	−30.1	137	5.1
$(1-x)CH_3(CH_2)_2COCH_3+xDMSO$	3071	−199	155	6.7
$(1-x)CH_3(CH_2)_3COCH_3+xDMSO$	3558	−505	505	3.3
$(1-x)CH_3(CH_2)_4COCH_3+xDMSO$	4341	−764	615	7.3
$(1-x)CH_3(CH_2)_5COCH_3+xDMSO$	4675	−1049	1016	8.1
$(1-x)CH_3(CH_2)_6COCH_3+xDMSO$	5224	−1189	1479	8.6
$(1-x)C_6H_5COCH_3+xDMSO$	1889	−61.4	−147.2	2.5

Table 3 Excess partial molar enthalpies at infinite dilution at 298.15 K

Systems	$H_1^{E,\infty}$/kJ mol^{-1}	$H_2^{E,\infty}$/kJ mol^{-1}
CH_3COCH_3 (1)+MMTSO (2)	1.32	1.95
$CH_3CH_2COCH_3$ (1)+MMTSO (2)	1.64	2.55
$CH_3(CH_2)_2COCH_3$ (1)+MMTSO (2)	2.31	3.03
$CH_3(CH_2)_3COCH_3$ (1)+MMTSO (2)	3.01	3.41
$CH_3(CH_2)_4COCH_3$ (1)+MMTSO (2)	3.82	3.94
$CH_3(CH_2)_5COCH_3$ (1)+MMTSO (2)	4.49	4.13
$CH_3(CH_2)_6COCH_3$ (1)+MMTSO (2)	5.36	4.82
CH_3COCH_3 (1)+DMSO (2)	1.56	1.72
$CH_3CH_2COCH_3$ (1)+DMSO (2)	2.28	2.22
$CH_3(CH_2)_2COCH_3$ (1)+DMSO (2)	3.42	3.03
$CH_3(CH_2)_3COCH_3$ (1)+DMSO (2)	4.57	3.56
$CH_3(CH_2)_4COCH_3$ (1)+DMSO (2)	5.72	4.19
$CH_3(CH_2)_5COCH_3$ (1)+DMSO (2)	6.74	4.64
$CH_3(CH_2)_6COCH_3$ (1)+DMSO (2)	7.93	5.48

$H_1^{E,\infty}$ – excess partial molar enthalpy of aliphatic ketones into sulfoxides at infinite dilution, $H_2^{E,\infty}$ – excess partial molar enthalpy of sulfoxides into aliphatic ketones at infinite dilution

proach, all molecules were treated as spherical molecules. The values of r for each system were calculated by (r_1+r_2). Here, r_1 and r_2 was the molecular radius of components 1 and 2. Those were calculated from the volume in the fourth column of Table 4. Not all of the dipole moments and other physico-chemical properties of 2-alkanone have been reported. The dipole moments and other physico-chemical properties of 2-alkanone were calculated by HyperChem [23] after geometrical optimization of the molecular shapes as shown in Ta-

ble 4. Geometrical optimization of the molecular shapes of these isomers was carried out by calculations using the Gaussian method [25] and Molecular Modeling Pro [26]. And ab initio calculations on molecules were performed at the RHF/6-311G level of theory.

Correlations between partial molar enthalpies at infinite dilution and dipole–dipole interaction and dipole–induced dipole interaction are shown in Figs 6 and 7, respectively. Partial molar enthalpies at infinite dilution decreased with increasing stabilization by

Table 4 Calculated physical properties of aliphatic ketones and sulfoxides

Sample	$10^{30} \mu$/C m	$10^3 \alpha$/nm^3	$10^3 V$/nm^3	r/nm
2-propanone	10.48	6.37	123.0	0.308
2-butanone	10.04	8.20	149.5	0.329
2-pentanone	9.71	10.04	178.5	0.349
2-hexanone	9.89	11.87	206.2	0.366
2-heptanone	9.77	13.71	233.8	0.382
2-octanone	9.75	15.54	261.5	0.397
2-nonanone	9.62	17.37	289.0	0.410
MMTSO	11.99	9.85	169.6	0.343
DMSO	15.05	5.01	118.4	0.305

μ – dipole moment, V – molecular volume, r – molecular radius, α – polarizability
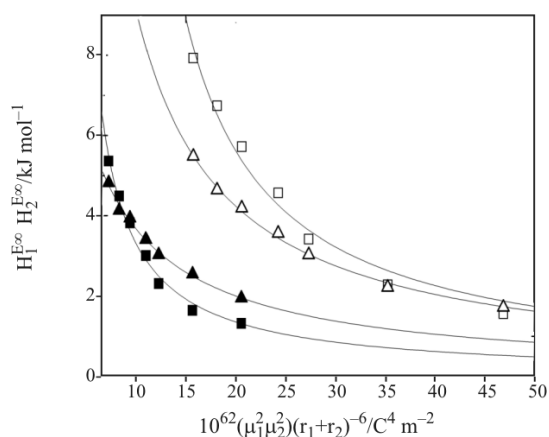

Fig. 6 Correlation between excess partial molar enthalpies at infinite dilution and $\mu_1^2\mu_2^2/(r_1+r_2)^6$ of aliphatic ketones(1)+sulfoxides(2): ■ – $H_1^{E,\infty}$ of ketones(1)+MMTSO(2), ▲ – $H_2^{E,\infty}$ of ketones(1)+MMTSO(2), □ – $H_1^{E,\infty}$ of ketones(1)+DMSO(2), △ – $H_2^{E,\infty}$ of ketones(1)+DMSO(2)

dipole–dipole or dipole–induced dipole interaction between 2-alkanone and sulfoxides. The correlations between partial molar enthalpies at infinite dilution and dipole–dipole interaction or dipole–induced dipole interaction were not linear. The correlations are summarized as Eq. (5).

$$H_i^{E,\infty} = \frac{B_i}{A_i + |u_{12,DX}|} \quad (5)$$

where, the subscript of DX in Eq. (5) is DD or DI. DD and DI show interaction energy of dipole–dipole and dipole–induced dipole, respectively. The coefficients of Eq. (5) for the systems and the standard deviations are listed in Tables 5 and 6. Coefficient A might be same unit of u_{12} from Eq. (5). u_{12} was calculated for pair interaction energy in a vacuum by a quantum mechanical method. So, coefficients A might contain interaction energy except pair interaction energy in a vacuum. When A was large and negative, partial molar enthalpies at infinite dilution showed large
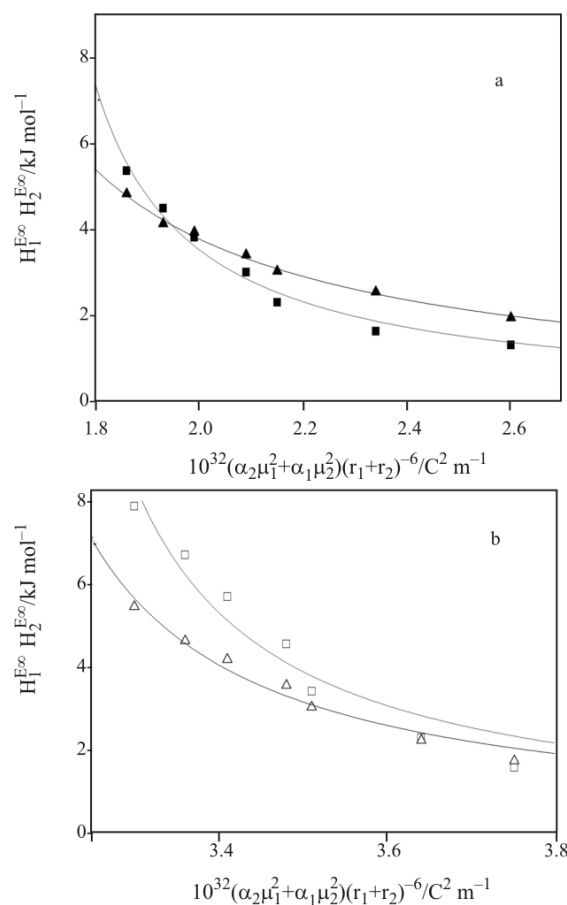

Fig. 7 Correlation between excess partial molar enthalpies at infinite dilution and $(\alpha_2\mu_1^2+\alpha_1\mu_2^2)/(r_1+r_2)^6$ of aliphatic ketones+sulfoxides: a – partial molar enthalpies of ketones(1)+MMTSO(2), b – partial molar enthalpies of ketones(1)+DMSO(2), ■,□ – $H_1^{E,\infty}$, ▲,△ – $H_2^{E,\infty}$

dependence on u_{12} and *vice versa*. Here, coefficients A of $H_1^{E,\infty}$ were more negative than $H_2^{E,\infty}$ for each system as shown in Tables 5 and 6. This means that partial molar enthalpies at infinite dilution of 2-alkanone might be largely affected by other

Table 5 Best-fit values for the coefficients of Eq. (5) for dipole-dipole interaction term $u(d–d)$ with the standard deviations of the fits

		$10^{62} A/$ J^2	$10^{59} B/$ $J^3\ mol^{-1}$	r^2	$s_f/$ $kJ\ mol^{-1}$
MMTSO	$H_1^{E,\infty}$	−3.07	22.96	0.989	0.17
	$H_2^{E,\infty}$	2.02	44.14	0.994	0.08
DMSO	$H_1^{E,\infty}$	−6.48	75.84	0.981	0.35
	$H_2^{E,\infty}$	−1.36	78.93	0.997	0.09

$u(d–d)$, dipole–dipole interaction $\mu_1^2 \mu_2^2/(r_1+r_2)^6$; r^2 – correlation coefficient; s_f – standard deviations of the fits

Table 6 Best-fit values for the coefficients of Eq. (5) for dipole-induced dipole interaction $u(d–i)$ with the standard deviations of the fits

		$10^{32} A/$ J	$10^{29} B/$ $J^2\ mol^{-1}$	r^2	$s_f/$ $kJ\ mol^{-1}$
MMTSO	$H_1^{E,\infty}$	−1.61	1.36	0.9874	0.22
	$H_2^{E,\infty}$	−1.33	2.53	0.9948	0.08
DMSO	$H_1^{E,\infty}$	−3.13	1.44	0.9374	0.64
	$H_2^{E,\infty}$	−3.05	1.42	0.9718	0.25

$u(d–i)$, dipole–induced dipole interaction $(\alpha_2 \mu_1^2 + \alpha_1 \mu_2^2/(r_1+r_2)^6$; r^2 – correlation coefficient; s_f – standard deviations of the fits

interaction energy except for pair interaction energy in a vacuum.

On the other hand, Eq. (5) can be expressed as Eq. (6):

$$H_i^{E,\infty}(A_i + |u_{12,DX}|) = B_i = \text{constant} \qquad (6)$$

As shown in Table 5, coefficients B_i of dipole–dipole interaction for DMSO systems in Eq. (6) were larger than those of the MMTSO system. Large coefficients of B might be shown that a product of pair interactions from dipole–dipole interaction between sulfoxides and 2-alkanone largely affect the stability of the systems because DMSO molecules (dipole moment: $13.4 \cdot 10^{-30}$ C m) have larger dipolar stabilization than MMTSO molecules ($10.7 \cdot 10^{-30}$ C m) in pure liquid state. In addition, coefficients B_i of dipole–induced dipole interaction for MMTSO and DMSO systems in Eq. (6) were smaller than 10 and 2%, respectively. The results might show that the effects of dipole–induced dipole interaction terms between sulfoxides and 2-alkanone are not very significant.

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