

**THERMODYNAMICS OF LIQUID MIXTURES CONTAINING METHYL METHYLTHIOMETHYL SULFOXIDE. V. EXCESS ENTHALPIES OF (DEUTEROCHLOROFORM + METHYL METHYLTHIOMETHYL SULFOXIDE), (DEUTEROCHLOROFORM + DIMETHYL SULFOXIDE) AND (DEUTEROCHLOROFORM + CHLOROFORM) AT 298.15 K \***

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ABSTRACT

The molar excess enthalpies  $H_m^E$  of the title mixtures have been determined by using a twin-microcalorimeter of the heat-conduction type which requires only 10 cm<sup>3</sup> of each component liquid for a series of runs over the whole range of mole fractions. The  $H_m^E$  of CDCl<sub>3</sub> + CHCl<sub>3</sub> is nearly athermal and its maximum value is 9 J mol<sup>-1</sup>. The  $H_m^E$  of CDCl<sub>3</sub>(1) + CH<sub>3</sub>SOCH<sub>2</sub>SCH<sub>3</sub>(2) and DMSO(2) are exothermic. The minimum values of  $H_m^E$  are -2.27 kJ mol<sup>-1</sup> at  $x_2 = 0.4$  for the former mixture and -2.91 kJ mol<sup>-1</sup> at  $x_2 = 0.4$  for the latter. An equilibrium constant  $K_1$  expressed in terms of mole fractions and standard enthalpy  $\Delta H_1^\ominus$  of formation of a 1:1 associated complex between CDCl<sub>3</sub> and CH<sub>3</sub>SOCH<sub>2</sub>SCH<sub>3</sub> have been evaluated to be  $K_1 = 3.8$  and  $\Delta H_1^\ominus$  (101325Pa) = -6.6 kJ mol<sup>-1</sup>, by assuming an ideal mixture of CDCl<sub>3</sub>, CH<sub>3</sub>SOCH<sub>2</sub>SCH<sub>3</sub> and their 1:1 and 2:1 associated complexes. The enthalpic stabilization on hydrogen bonding between CDCl<sub>3</sub> and CH<sub>3</sub>SOCH<sub>2</sub>SCH<sub>3</sub> molecules is smaller than that between CHCl<sub>3</sub> and CH<sub>3</sub>SOCH<sub>2</sub>SCH<sub>3</sub> molecules by about 23%.

INTRODUCTION

Methyl methylthiomethyl sulfoxide (MMTSO), CH<sub>3</sub>SOCH<sub>2</sub>SCH<sub>3</sub>, may be used as a good solvent for various kinds of substances because of its characteristic molecular structure, which consists of a hydrophilic part having large polarization and lipophilic parts.

A series of thermodynamic measurements for binary mixtures containing MMTSO or a related compound were carried out by the present authors, to

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clarify the correlation between the thermodynamic properties of such mixtures and the molecular structures of their components. In our previous papers [1–3], the excess thermodynamic functions for the systems MMTSO + water, + benzene, + dimethyl sulfoxide (DMSO), + carbon tetrachloride, + chloroform, and + dichloromethane are reported.

The purpose of this paper is the presentation of excess enthalpies for the title mixtures at 298.15 K with the aim of obtaining information about the isotope effect on hydrogen bonding.

## EXPERIMENTAL

### *Materials*

The method of purification and the purities of MMTSO (Nippon Soda Co.), DMSO (Merck, Uvasol) and chloroform (Merck, Uvasol) were the same as those described previously [1,2,3]. Deuteriochloroform (stated deuterium content not less than 99.95%, Merck, for FT-NMR) was used without further purification.

The coulometric Karl-Fischer's method using a Mitsubishi Moisture meter model CA-02 (Mitsubishi Chemical Ind.) gave the water content of the deuteriochloroform to be 0.01 mol% or less.

### *Apparatus and procedures*

A twin-microcalorimeter of the heat-conduction type (laboratory designation MC-AII) [4,5] which requires only 10 cm<sup>3</sup> of each component for a series of runs over the range of mole fractions was used for the measurements of excess enthalpies. An automatically measuring, on-line system was used. A schematic illustration of the calorimeter system used is shown in Fig. 1.

A couple of thermopiles (Melcor, CP 1.4-71-10) were used as temperature sensors in the calorimeter [4,6]. The e.m.f. produced was amplified by a d.c. amplifier (Ohkura, Model AM1002) to 10 V, which was connected to an

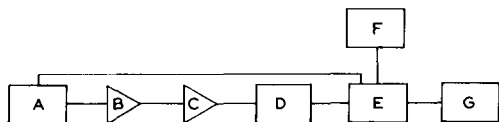


Fig. 1. Block diagram of the measuring system: A, twin-microcalorimeter; B, d.c. amplifier (Ohkura, AM 1002); C, isolation amplifier (Mtt Co. MS-3204); D, A/D converter (Datel, ADC-HZ12BGC); E, microcomputer (NEC, PC-9801F); F, CRT display (NEC, PC-8851); G, printer (Epson, UP-130K).

A/D converter (Datel, ADC-HZ12BGC) through an isolation amplifier (Mtt Co., Model MS-3204). A digital reading was sampled on the A/D converter for every 100  $\mu$ s. The numerical values accumulated every 256 readings [7] were fed into a RAM of a microcomputer (NEC, Model PC-9801F) and stored on a floppy disk after completion of the measurements.

The attainment of thermal equilibrium between samples and the calorimeter system was checked by the fact that the difference of the e.m.f. of the thermopiles in the measuring sample side and the reference sample side approached very small values (corresponding to ca.  $5 \times 10^{-6}$  K). After thermal equilibrium was attained, mixing was started and completed by ten slow rocking motions of the mixing vessels in mercury pools. This procedure of rocking the vessels was repeated at least three times until the reproducibility of the heat of stirring obtained was less than 0.1%.

The temperature difference was integrated with respect to time by the method of Simpson to obtain the enthalpy change on mixing. The points of starting and ending of enthalpy change were determined by the initial deviation from and contact with a base line which was predicted by the method of least squares. The tests of the reproducibility of enthalpy measurements were carried out with known amounts of Joule's heat supplied [4], which ranged from 20 to 0.1 J, and the uncertainty of the measurement was less than 0.02%.

## RESULTS AND DISCUSSION

The experimental excess enthalpies obtained are summarized in Table 1. They were fitted to eqn. (1) by the method of least squares. The selection of the number of terms was determined by the best fit of the experimental results.

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

The coefficients  $A_i$  adopted are listed in Table 2, along with the calculated standard deviations of the fit  $s_f$ . The observed values and the smoothed ones (shown as curves) are presented in Figs. 2 and 3, together with literature values [3,8,9] for comparison.

As shown in Fig. 2, the excess molar enthalpy of  $\text{CDCl}_3 + \text{CHCl}_3$  is nearly athermal and its maximum value is  $9 \text{ J mol}^{-1}$ . It is much smaller than the value of  $33 \text{ J mol}^{-1}$  for  $\text{D}_2\text{O} + \text{H}_2\text{O}$  [10].

The only available literature value for this mixture is  $4 \text{ J mol}^{-1}$  for the heat of solution per mole of  $\text{CDCl}_3$  observed by Duer and Bertrand [9], when some 10–15 ml of  $\text{CDCl}_3$  was added to ca. 300 ml of  $\text{CHCl}_3$ . It

TABLE 1

Experimental excess enthalpies at 298.15 K

$x$	$H_m^E$ (J mol <sup>-1</sup> )	$x$	$H_m^E$ (J mol <sup>-1</sup> )	$x$	$H_m^E$ (J mol <sup>-1</sup> )
$(1-x)\text{CDCl}_3 + x\text{MMTSO}$					
0.03036	-353.2	0.03716	-413.8	0.08386	-883.2
0.1035	-1065.5	0.1725	-1585.1	0.2362	-131.5
0.2970	-2153.0	0.4109	-2268.1	0.4743	-222.9
0.5356	-2086.3	0.6192	-1806.6	0.7114	-1436.6
0.7223	-1386.4	0.7306	-1346.0	0.7553	-124.2
0.8359	-822.3	0.8414	-799.3	0.9412	-291.1
0.9647	-195.2	0.9652	-177.2		
$(1-x)\text{CDCl}_3 + x\text{DMSO}$					
0.05345	-670.8	0.1195	-1419.3	0.1538	-1755.2
0.1863	-2042.6	0.2058	-2206.7	0.2281	-2357.2
0.2985	-2738.0	0.3674	-2896.0	0.3836	-2919.1
0.4984	-2799.0	0.5536	-2579.9	0.6222	-2248.2
0.7021	-1798.6	0.7298	-1601.1	0.8181	-1606.0
0.8600	-791.0	0.9201	-443.9	0.9223	-430.6
0.9628	-193.8	0.9822	-86.60		
$(1-x)\text{CDCl}_3 + x\text{CHCl}_3$					
0.09992	3.70	0.1107	3.81	0.2224	7.07
0.3788	8.44	0.4422	8.87	0.4994	8.78
0.6183	7.21	0.6425	7.26	0.7670	4.63
0.8798	2.68				

corresponds to ca. 0.2 J mol<sup>-1</sup> of excess molar enthalpy at 0.95–0.97 mole fraction of chloroform. Our value calculated at the same mole fraction amounts to 0.66–1.00 J mol<sup>-1</sup> of excess molar enthalpy.

For the mixtures  $\text{CDCl}_3 + \text{MMTSO}$  and  $\text{CHCl}_3 + \text{MMTSO}$ , the amounts of evolved heat were smaller than those for  $\text{CDCl}_3 + \text{DMSO}$  and  $\text{CHCl}_3 +$

TABLE 2

Best-fit values for the coefficients  $A_i$  of eqn. (1) and the calculated standard deviations of the fit  $s_f$ 

System	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$s_f$ (J mol <sup>-1</sup> )
$\text{CDCl}_3 + \text{MMTSO}$	-8671.1	-4179.2	119.7	870.2	-	7.1
$\text{CHCl}_3 + \text{MMTSO}$	-8955.7	-4516.9	-750.2	1236.6	-	7.5 <sup>a</sup>
$\text{CDCl}_3 + \text{DMSO}$	-11085.1	-5785.2	1571.9	1893.2	703.7	9.8
$\text{CHCl}_3 + \text{DMSO}$	-11237	-6330	1070	2392	96	11.0 <sup>b</sup>
$\text{CDCl}_3 + \text{CHCl}_3$	34.36	10.61	-3.60	-	-	0.2

<sup>a</sup> Cited for comparison from Kimura et al. [3].<sup>b</sup> Cited for comparison from Joly and Philippe [8].

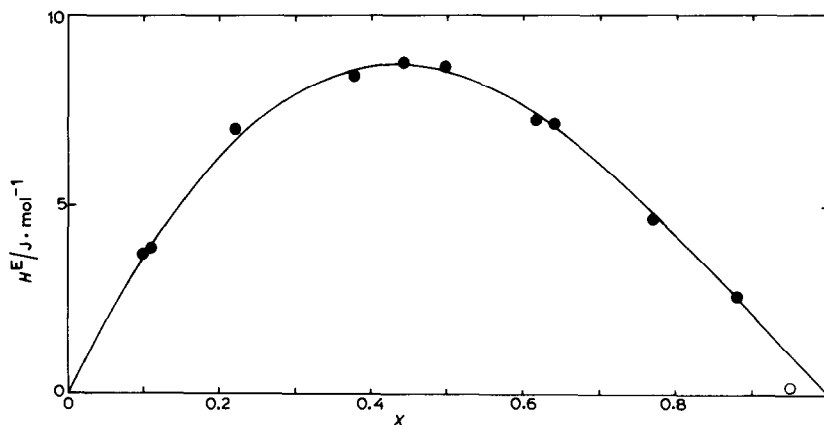


Fig. 2. Excess enthalpies of  $(1-x)\text{CDCl}_3 + x\text{CHCl}_3$  at 298.15 K: ●, observed values; —, calculated from eqn. (1); ○, literature value [9].

DMSO. The former is about 3/4 of the latter. The main reason for this might be the weakening of the hydrogen bonding between  $\text{CDCl}_3$  or  $\text{CHCl}_3$  and  $\text{>S=O}$  of MMTSO molecules due to the existence of a  $-\text{CH}_2-\text{S}-\text{CH}_3$  radical in an MMTSO molecule [1-3].

Figure 3 also shows that the evolved heats for all the mixtures skew slightly to the chloroform- or deuteriochloroform-rich region and shows an inflexion-point on each curve of  $\text{CDCl}_3 + \text{DMSO}$  and  $\text{CHCl}_3 + \text{DMSO}$  at about 80 mol%.

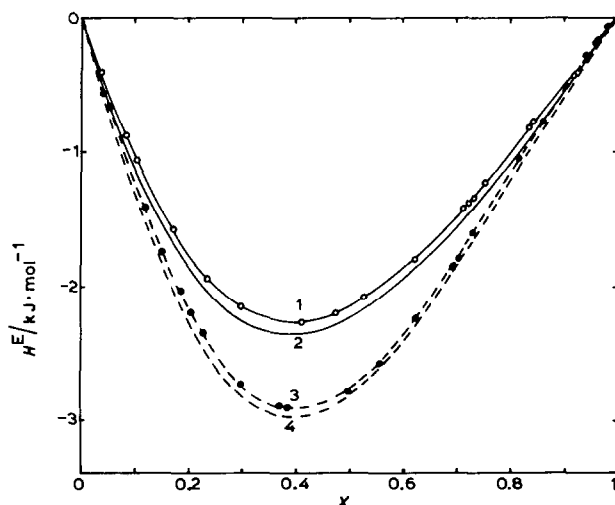


Fig. 3. Excess enthalpies at 298.15 K: 1,  $(1-x)\text{CDCl}_3 + x\text{MMTSO}$ ; 2,  $(1-x)\text{CHCl}_3 + x\text{MMTSO}$  [3]; 3,  $(1-x)\text{CDCl}_3 + x\text{DMSO}$ ; 4,  $(1-x)\text{CHCl}_3 + x\text{DMSO}$  [8].

TABLE 3

Limiting partial molar excess enthalpies  $H_1^{E,\infty}$  and  $H_2^{E,\infty}$  at infinite dilution at 298.15 K obtained from eqn. (1) with the coefficients from Table 2

System	$H_1^{E,\infty}$ ( $x_2 \approx 1$ ) (kJ mol <sup>-1</sup> )	$H_2^{E,\infty}$ ( $x_2 \approx 0$ ) (kJ mol <sup>-1</sup> )
CDCl <sub>3</sub> (1)+MMTSO(2)	-5.2	-12
CHCl <sub>3</sub> (1)+MMTSO(2)	-6.4	-13
CDCl <sub>3</sub> (1)+DMSO(2)	-4.9	-13
CHCl <sub>3</sub> (1)+DMSO(2)	-6.1	-14
CDCl <sub>3</sub> (1)+CHCl <sub>3</sub> (2)	0.020	0.041

The limiting values of  $H_1^{E,\infty}$  and  $H_2^{E,\infty}$  at infinite dilution, calculated from eqn. 1 with the parameters in Table 2, are listed in Table 3. The isotope effects of deuterium on the excess molar enthalpies for the MMTSO mixture and the DMSO one were the same. Namely the change of CHCl<sub>3</sub> to CDCl<sub>3</sub> caused about 1 kJ mol<sup>-1</sup> reduction in every evolved heat. These differences may arise from the difference of stabilization on hydrogen bonding with the sulfoxides between CDCl<sub>3</sub> and CHCl<sub>3</sub>. A similar result was reported by Handa et al. [12] for triethylamine + CDCl<sub>3</sub> and triethylamine + CHCl<sub>3</sub>.

By using the ideal associated solution model [3,11], an equilibrium constant and enthalpy of formation of a 1:1 complex of MMTSO and deuteriochloroform were determined, assuming the following equilibria



where S and C are MMTSO and deuteriochloroform, respectively. Equilibrium constants  $K_1$  and  $K_2$  for eqns. (2) and (3) and the standard

TABLE 4

Comparison of the thermodynamic quantities for 1:1 and 1:2 complex formation of MMTSO and CDCl<sub>3</sub> with those of MMTSO and CHCl<sub>3</sub> at 298.15 K and 101325 Pa

	CDCl <sub>3</sub>	CHCl <sub>3</sub> [3]
(1:1 complex)		
$K_1$	3.8	2.2
$\Delta H_1^\ominus$ (kJ mol <sup>-1</sup> )	-6.6	-8.7
$\Delta G_1^\ominus$ (kJ mol <sup>-1</sup> )	-3.3	-2.0
$\Delta S_1^\ominus$ (J K <sup>-1</sup> mol <sup>-1</sup> )	-11	-23
(1:2 complex)		
$K_2$	3.1	4.4
$\Delta H_2^\ominus$ (kJ mol <sup>-1</sup> )	-16	-12
$\Delta G_2^\ominus$ (kJ mol <sup>-1</sup> )	-2.8	-3.7
$\Delta S_2^\ominus$ (J K <sup>-1</sup> mol <sup>-1</sup> )	-45	-28

enthalpies of complex formation  $\Delta H_1^\ominus$  and  $\Delta H_2^\ominus$  were evaluated by the same calculation and assumption as those reported earlier [3], and summarized in Table 4.

Of those values the thermodynamic quantities for 1 : 1 complex formation may be reliable, since the assumption may hold near the infinite dilution of  $\text{CDCl}_3$ , although an MMTSO molecule has three proton- or deuterium-accepting sites [3]. Similar calculation could not be achieved for  $\text{DMSO} + \text{CDCl}_3$  because of the existence of a point of inflexion on the  $H_m^E$  vs.  $x_2$  curve in the dilute range of  $\text{CDCl}_3$  mole fraction, as shown in Fig. 3.

Enthalpic stabilization by hydrogen bonding for 1 : 1 complex formation between  $\text{CDCl}_3$  and MMTSO is smaller than that of  $\text{CHCl}_3$  and MMTSO by about  $2 \text{ kJ mol}^{-1}$  (ca. 23%). However, the entropic unstabilization ( $T\Delta S_1$ ) for the former is smaller than that for the latter by about  $3.6 \text{ kJ mol}^{-1}$  (ca. 52%).

Consequently abundance of the 1 : 1 complex for  $\text{MMTSO} + \text{CDCl}_3$  is larger than that for  $\text{MMTSO} + \text{CHCl}_3$  in dilute solution at 298.15 K.

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