論 文

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Thermodynamics of Liquid Mixtures Containing Methyl Methylthiomethyl Sulfoxide. II.[1] Excess Enthalpies of (Water +, Benzene +, Dimethyl Sulfoxide + Methyl Methylthiomethyl Sulfoxide) and (Water +, Benzene + Dimethyl Sulfoxide) at 298.15 and 318.15 K.

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To study the relation between molecular structure of components and properties of the mixtures containing methyl methylthiomethyl sulfoxide (MMTSO), $CH_3(CH_3SCH_2)SO$, excess molar enthalpies of the title mixtures have been determined over the whole range of mole fraction by using a twin-microcalorimeter of heat-conduction type. The excess enthalpies obtained for the mixtures of MMTSO show similar tendencies to those of DMSO. The mixture (DMSO + MMTSO) has been found to be nearly athermal. Derived excess partial molar enthalpy of benzene of $\{(1-x)$benzene $+ x$MMTSO$\}$ at 298.15 K shows a maximum at $x=0.91$. The minima of excess partial molar enthalpy of water observed at $x=0.62$ (at 298.15 K) and 0.71 (at 318.15 K) for $\{(1-x)$water $+ x$MMTSO$\}$ are discussed, as well as those observed at $x=0.77$ (at 298.15 K) and 0.73 (at 318.15 K) for $\{(1-x)$water $+ x$DMSO$\}$. Measurements on the present apparatus require only 15 cm^3 of each component for a series of runs of one mixture over the whole range of mole fraction at a temperature.

1. Introduction

Methyl methylthiomethyl sulfoxide (MMTSO), $CH_3(CH_3SCH_2)SO$, first synthesised by Ogura and Tsuchihashi,[2–4] is a compound which may be used as a universal solvent. A series of thermodynamic measurements are being undertaken for binary mixtures containing MMTSO or related compound by the present authors, to study the correlation between thermodynamic properties of such mixtures and molecular structures of their components.

In this paper, excess molar enthalpies of the mixtures of MMTSO have been reported and compared with those of DMSO over the whole range of mole fraction. The excess enthalpy of (DMSO + MMTSO) is also discussed as a reference system of the comparison.

2. Experimental

Materials

MMTSO was kindly supplied by Dr. Ogura**, Sagami Chemical Research Center, Kanagawa and Nippon Soda Co., Ltd. (stated purity: better than 99 per cent) by the courtesy of Dr. Tayagaki. The samples were dried with calcium hydride and distilled through a vacuum-jacketed Vigreux column under reduced pressures, by admitting a fine stream of dry nitrogen and then degassed. The vacuum distillation was repeated. The middle cut was recrystallized fractionally five times and then fractionally distilled through the Vigreux column twice at temperatures lower than 365 K under reduced pressures by introducing dry nitrogen.

The samples of DMSO, benzene, and water used were purified as described in our preceding paper.[1] The purification procedures of mercury were the same as those described earlier.[5]

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The coulometric Karl Fischer's method on Mitsubishi Moisture Meter model CA-05 (Mitsubishi Chemical Ind., Ltd.) gave the water content of the final samples to be 0.004, 0.003, and 0.0014 moles per cent, respectively, for MMTSO, DMSO, and benzene. The purities determined by d.s.c.[6] (Daini Seikosha model SSC/560) for MMTSO, DMSO, and benzene were not less than 99.99 moles per cent. All the mixtures were prepared by mass.

Apparatus and procedures

A twin-microcalorimeter of heat-conduction type[7] was used for the measurements of excess enthalpies. Teflon vessels for enthalpy-of-solution measurement[7] were replaced with mixing vessels[8] mounted on assemblies for enthalpy-of-mixing measurement, where the vessels were immersed into mercury in vessel holders.[8] Mercury was used as heat-conducting medium.

Mixing and stirring were carried out manually. Rocking was made eight to ten times for each stirring but 20 times for viscous mixtures of (DMSO + MMTSO). The procedures used for loading the samples into the vessels and measuring heats were similar to those used for the measurement of enthalpy of dilution on a rocking twin-microcalorimeter of heat-conduction type (laboratory designation: RMC-II),[5] but the capacities of the present mixing vessels were much smaller than those for RMC-II. Consequently, only 15 cm^3 of each component was sufficient for a series of runs of one system over the whole range of mole fraction at a temperature in this work.

3. Results and Discussion

Experimental results and their reliability

The experimental results of excess enthalpies obtained are summarised in Table 1. They were fitted with either Eq. (1) or (2)[9,10] by the method of least squares.

$$\frac{H_m^E}{J\cdot mol^{-1}} = x_1 x_2 \sum_{i=1}^{k} A_i (x_2 - x_1)^{i-1} \qquad (1)$$

$$\frac{H_m^E}{J\cdot mol^{-1}} = x_1 x_2 \sum_{i=1}^{k} A_i (x_i^{1/2})^{i-1} \qquad (2)$$

The selection of the equation and the number of the coefficients were made so that standard deviation from the fit, s_f, may be minimal. The coefficients A_i determined are listed in Table 2, as well as the values of s_f. The observed values and the smoothed ones (shown as curves) are presented in Figs. 2 to 6, together with literature values.[11-13]

Fig. 2 shows good agreement in the excess enthalpy for (benzene + DMSO) at 298.15 K among the values of present authors, Tanaka *et al.*,[11] and Fenby *et al.*[12] The earlier values of Kenttämaa *et al.*[13] are higher than the present results in benzene-rich region, but agreement is reasonable. The present results agreed with those of Fenby *et al.*[12] within ±1 per cent deviation as shown in Fig. 1, although their smoothed values deviate significantly from the present one. The 1 per cent deviation is compared with the maximum imprecision of the present measurements (±1 per cent or less). Such a rather large uncertainty might be introduced during the injection of sample liquids into the mixing vessels, because the amounts of the samples loaded in a run range from 1 cm^3/1 cm^3 to 1.2 cm^3/0.2 cm^3 in this work.

Discussion for the benzene mixtures

For the both (benzene + MMTSO) and (benzene + DMSO) systems, values of H_m^E are positive and nearly symmetrical with respect to the mole fraction. Strictly speaking, those for (benzene + MMTSO) skew slightly in MMTSO-rich region showing a point of inflection at 298.15 K (Fig. 3).

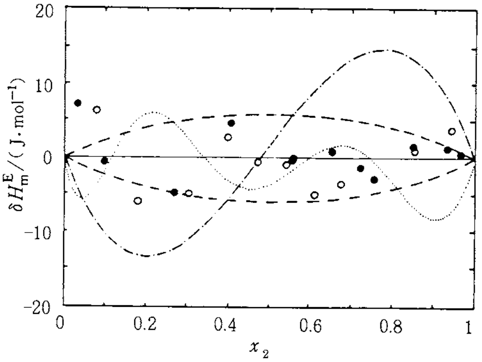

Fig. 1 Plots of the deviations: $\delta H_m^E = \{H_m^E$ (expt.) $- H_m^E$ (eq. 1)$\}$ for {benzene(1) + DMSO(2)} at 298.15 K. Experimental results: ●, present work; ○, Fenby *et al.*[12] ··········, Calculated from the smoothing equation of Tanaka *et al.*,[11] their experimental values being located along the dotted curve; —·—·—, calculated from the smoothing equation of Fenby *et al.*;[12] - - - - - -, ±1 per cent deviation.

Table 1. Experimental excess enthalpies at 298.15 and 318.15 K

x_2	H_m^E / $J \cdot mol^{-1}$	x_2	H_m^E / $J \cdot mol^{-1}$
water(1) + MMTSO(2) at 298.15 K			
0.01435	−147.0	0.02968	−282.0
0.03004	−290.9	0.04741	−418.8
0.06471	−517.5	0.06600	−506.4
0.07043	−544.4	0.1338	−816.3
0.1441	−831.1	0.1544	−859.7
0.2450	−1040.9	0.2626	−1060.7
0.2776	−1066.2	0.3481	−1070.4
0.3534	−1078.9	0.3780	−1065.0
0.4163	−1043.5	0.4711	−991.3
0.5361	−892.1	0.5852	−807.9
0.6914	−609.3	0.6915	−602.1
0.7303	−519.9	0.8165	−354.6
0.8695	−246.2	0.9312	−139.6
0.9476	−105.5	0.9763	−61.9
water(1) + MMTSO(2) at 318.15 K			
0.008772	−87.6	0.01654	−155.3
0.01945	−170.9	0.03282	−271.9
0.03460	−286.7	0.05643	−429.7
0.05654	−431.4	0.07011	−497.5
0.07840	−548.6	0.1142	−702.3
0.1363	−765.9	0.1445	−785.6
0.1464	−804.8	0.1560	−832.5
0.1663	−857.0	0.1683	−868.2
0.1767	−860.0	0.1837	−915.0
0.1866	−908.6	0.2492	−1008.4
0.2793	−1034.3	0.3347	−1039.5
0.3937	−1019.4	0.4533	−964.3
0.4759	−937.4	0.5386	−845.1
0.7248	−473.2	0.7300	−488.9
0.8908	−176.8	0.8947	−161.3
0.9468	−75.9	0.9594	−62.1
0.9813	−27.4	0.9843	−14.7
benzene(1) + MMTSO(2) at 298.15 K			
0.02722	87.5	0.05561	178.9
0.1166	301.8	0.2420	475.5
0.2431	485.8	0.2654	502.6
0.3462	561.8	0.3506	557.5
0.4508	576.9	0.4746	574.6
0.5253	564.9	0.6343	509.9
0.7044	440.0	0.7524	379.2
0.8086	307.5	0.8774	202.7
0.9345	98.3	0.9639	56.6
benzene(1) + MMTSO(2) at 318.15 K			
0.01965	71.5	0.02820	87.1
0.04006	120.7	0.05599	170.3
0.08909	239.1	0.1072	278.4
0.1936	420.5	0.2288	462.2
0.2840	511.1	0.3482	549.8
0.3830	556.7	0.3960	561.0
0.4510	564.3	0.4606	566.7
0.4752	562.9	0.4834	560.8
0.4975	559.7	0.5934	517.6
0.6699	454.4	0.7346	392.0
0.7415	390.9	0.8242	277.6
0.8242	277.4	0.8588	226.4
0.9125	143.3	0.9220	125.4
0.9328	110.7	0.9740	40.9
DMSO(1) + MMTSO(2) at 298.15 K			
0.05038	5.0	0.09255	7.7
0.1704	10.5	0.2121	10.8
0.3266	13.1	0.4093	13.0
0.5228	12.0	0.6224	9.6
0.7332	6.0	0.8451	2.8
0.9024	1.6	0.9642	1.1
DMSO(1) + MMTSO(2) at 318.15 K			
0.07202	3.4	0.09442	4.4
0.2006	8.4	0.4169	10.4
0.4199	9.6	0.5224	9.7
0.5675	9.2	0.6323	7.4
0.6467	6.3	0.7805	2.8
water(1) + DMSO(2) at 298.15 K			
0.05950	−1035.0	0.1088	−1708.6
0.1480	−2122.3	0.2113	−2586.8
0.2490	−2773.4	0.5784	−2868.3
0.3444	−2961.0	0.4253	−2886.7
0.5294	−2547.8	0.5613	−2417.3
0.7181	−1566.8	0.7675	−1294.7
0.8403	−847.7	0.9127	−457.1
0.9520	−249.5		
water(1) + DMSO(2) at 318.15 K			
0.03232	−529.4	0.08945	−1312.4
0.09137	−1346.3	0.1005	−1468.8
0.1625	−2075.3	0.1978	−2338.7
0.2164	−2460.8	0.2706	−2689.3
0.2803	−2729.2	0.3069	−2759.5
0.3585	−2838.4	0.4299	−2759.5
0.5233	−2449.9	0.5639	−2263.6
0.5884	−2159.2	0.7618	−1255.0
0.7820	−1155.9	0.8277	−915.7
0.8835	−610.5	0.9415	−306.3
benzene(1) + DMSO(2) at 298.15 K			
0.03216	105.9	0.09781	256.6
0.2663	483.5	0.4070	575.4
0.5566	582.7	0.5585	582.6
0.6519	546.7	0.7210	490.5
0.7568	451.1	0.8528	317.4
0.9335	159.0	0.9682	78.9_7
benzene(1) + DMSO(2) at 318.15 K			
0.03454	109.7	0.06311	189.5
0.06859	202.1	0.08504	226.7
0.1489	338.5	0.1778	382.8
0.2539	459.4	0.3970	545.3
0.4169	553.6	0.4837	561.6
0.5840	536.1	0.6499	505.0
0.8002	379.1	0.8032	369.8
0.8464	307.7	0.9238	173.6
0.9440	136.4	0.9513	117.0

Table 2. Best-fit values of the coefficients A_i of Eq. (1), Eq. (2), or Eq. (3) and the calculated standard deviations of the fit s_f.

T/K	Eq.	A_1	A_2	A_3	A_4	A_5	s_f/J·mol^{-1}
			water(1) + MMTSO(2)				
298.15	(2)	−14686.2	38935.6	−65472.9	66112.8	−25806.1	6.8
318.15	(2)	−11986.8	22823.5	−32067.7	31724.1	−11856.9	7.9
			benzene(1) + MMTSO(2)				
298.15	(1)	2291.26	−401.14	187.49	−599.56		4.3
318.15	(1)	2248.16	391.42	13.031	557.17	313.22	4.5
			DMSO(1) + MMTSO(2)				
298.15	(1)	41.77	45.22	−46.35	89.72		0.5
	(3)	49.31	19.05	6.487	5.110		0.6
318.15	(1)	39.25	−27.53	−19.31	−4.969		0.4
	(3)	42.99	12.77	−24.78			0.5
			water(1) + DMSO(2)				
298.15	(1)	−10665.0	7363.1	−1753.4	177.87		6.0
318.15	(1)	−10172.6	7353.9	−1324.2	154.44		7.0
			benzene(1) + DMSO(2)				
298.15	(1)	2350.12	45.056	578.21	−438.15		3.1
318.15	(1)	2236.79	−29.918	356.98	−418.70	544.82	4.4

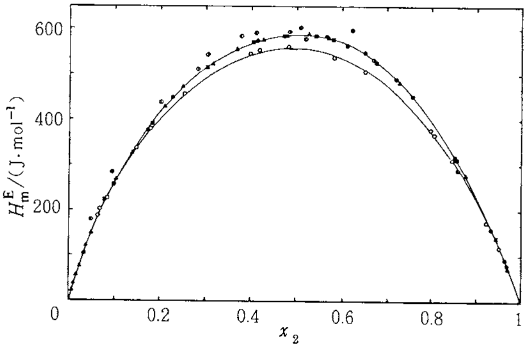

Fig. 2 Excess molar enthalpies of {benzene(1) + DMSO(2)} as a function of the mole fraction of DMSO: ●, this work; ▲, Tanaka *et al.*;[11] ■, Fenby *et al.*;[12] ⦶, Kenttämaa and Lindberg[13] at 298.15 K; and ○, this work at 318.15 K. Curves are least-squares representation of our results by Eq. (1).

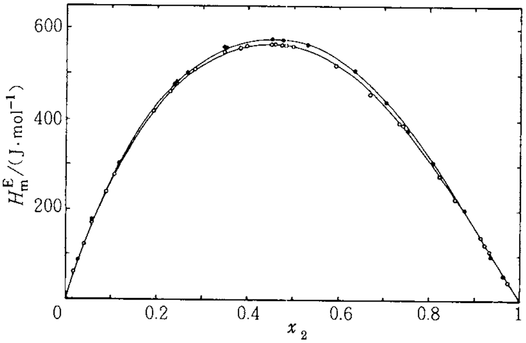

Fig. 3 Excess molar enthalpies of {benzene(1) + MMTSO(2)} as a function of mole fraction: ●, at 298.15 K; ○, at 318.15 K. The curves are least-squares representation of our results by Eq. (1).

Their temperature coefficients are negative for the both systems.

The main features of the H_m^E vs x curves can be explained by assuming that the absorption of heat on breakdown of strong and nonspecific[14] dipole-dipole interactions between molecules of DMSO (permanent dipole moment of the molecule: 14×10^{-30}C·m) or MMTSO (11×10^{-30}C·m) and that of quadrupolar attraction of ordered benzene molecules are partly compensated by the evolution of heat due to the dipole-induced dipole attraction between molecules of strongly polar DMSO or MMTSO and polarizable benzene, and additional stabilization arising from volume contraction on mixing.[1]

The excess partial molar enthalpy of benzene H_1^E of (benzene + MMTSO) shows a maximum at about $x = 0.9$ at 298.15 K and a break near $x = 0.8$ at 318.15 K as shown in Fig. 4, although

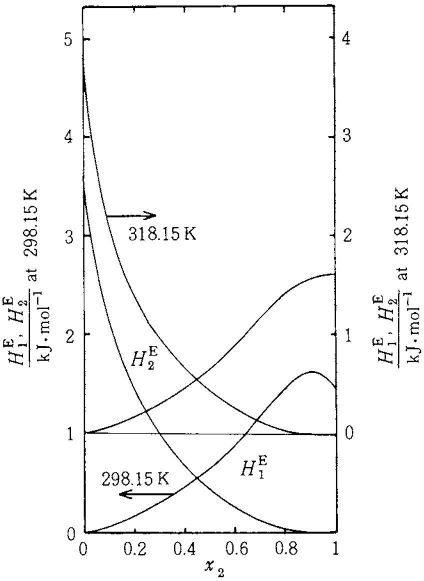

Fig. 4 Excess partial molar enthalpies for {benzene(1) + MMTSO(2)} at 298.15 and 318.15 K which are calculated by Eq. (1) and the coefficients in Table 2. H_1^E(max) and H_2^E(min) are 1.6_5 and -0.005 kJ·mol^{-1}, respectively at x_2(max) = 0.91_2 at 298.15 K.

the excess partial molar volume of benzene V_1^E shows a minimum at $x=0.9$ at 318.15 K and a break near $x=0.9$ at 298.15 K.[1] Since (benzene + DMSO) doesn't show such an anomaly, it may be assigned to the difference in molecular structures between MMTSO and DMSO, *i.e.*, existence of a flexible $-CH_2-S-CH_3$ chain in an MMTSO molecule.

Discussion for the (DMSO+MMTSO) system

The values of H_m^E for (DMSO + MMTSO) are positive and very small, as described in Fig. 5, with a maximum value of about 12 J·mol^{-1} at 298.15 K, but skewed significantly with a point of inflection in the MMTSO-rich region at each temperature. The temperature coefficient of H_m^E was negative.

Since V_m^E of this system is slightly positive and symmetrical with respect to the mole fraction and its temperature coefficient is negative as if the system were a regular mixture,[1] H_m^E is plotted against volume fraction of MMTSO using Eq. (3)

$$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}} = \phi_1\phi_2 \sum_{i=1}^{k} A_i (\phi_2-\phi_1)^{i-1} \qquad (3)$$

$$\frac{H_m^E}{\mathrm{J\cdot mol^{-1}}} = \phi_1\phi_2 \sum_{i=1}^{k} A_i (\phi_1^{1/2})^{i-1} \qquad (4)$$

in the upper part of Fig. 5, in order to see the effect of difference in molecular size (molar volume in this case). Although the best-fitted curves obtained have maxima at $\phi_2=0.5$, they skew in the MMTSO-rich region and the points of inflection do not disappear at both temperatures. We cannot fit the curves adequately to the experimental points by Eqs. (1)~(4) for this mixture. This asymmetry may arise from the difference in their molecular shape. In any case, nearly athermal H_m^E shows that the molecular interactions of like and unlike pairs of MMTSO and DMSO are nearly equal at these temperatures.

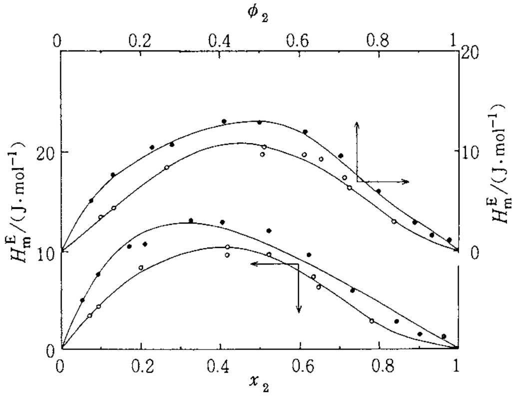

Fig. 5 Excess molar enthalpies of {DMSO(1) + MMTSO(2)} as a function of the mole fraction (lower ones) and those as a function of the volume fraction (upper ones) of MMTSO: ●, at 298.15 K; ○, at 318.15 K. The lines are calculated by Eq. (1) and (3) with the coefficients from Table 2.

Discussion for aqueous mixtures

The excess molar enthalpies H_m^E of (water + MMTSO) and (water + DMSO) are large and negative. Their temperature coefficients (excess molar heat capacities at constant pressure) are positive as shown in Figs. 6 and 7. The present results of H_m^E of (water + DMSO) at 298.15 K is compared with literature values[15-18] as shown in Fig. 7. The best agreement is obtained with the values of Fox and Whittingham,[15] and Kenttämaa and Lindberg.[17]

The excess partial molar enthalpies H_1^E of water in the aqueous mixtures show minima in

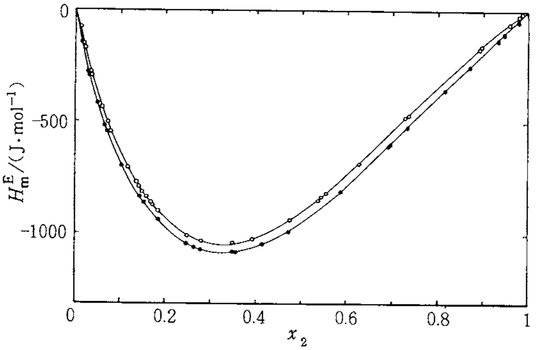

Fig. 6 Excess molar enthalpies of {water(1) + MMTSO(2)} as a function of mole fraction: ●, at 298.15 K; ○, at 318.15 K. The lines are calculated by Eq. (2) with the coefficients from Table 2.

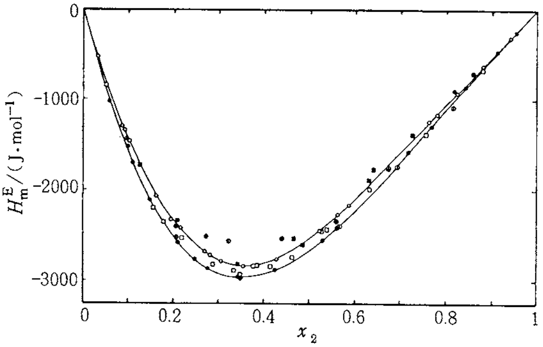

Fig. 7 Excess molar enthalpies of {water(1) + DMSO(2)} as a function of mole fraction: -●-, this work; □, Fox and Whittingham;15) ⦶, Cowie and Toporowski;16) ⊕, Kenttämaa and Lindberg;17) ■, Clever and Pigott;18) at 298.15 K and -○-, this work at 318.15 K. The lines are calculated by Eq. (1) with the coefficients from Table 2.

the sulfoxide-rich region as shown in Figs. 8 and 9. These minima tell us that the stabilization in enthalpy by addition of water into the mixture increases with the increase in the mole fraction of water until the H_1^E reaches the minimum in the sulfoxide-rich region. These situations may be explained, if we assume that the strength of an O–H ··· O hydrogen bond between a water molecule and the sulfoxide molecule is much stronger than that between water molecules and if we remember that a water molecule can form only one or two hydrogen bonds with the sulfoxide molecules instead of four bonds with neighbours

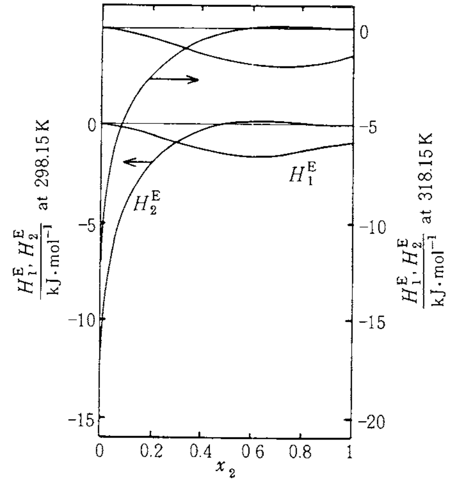

Fig. 8 Excess partial molar enthalpies of {water(1) + MMTSO(2)} at 298.15 and 318.15 K calculated by Eq. (2) with the coefficients from Table 2. H_1^E(min) and H_2^E(max) are respectively -1.6_5 and 0.15 $kJ\cdot mol^{-1}$ at x_2 (min) = 0.61_8 at 298.15 K and -1.9_6 and 0.07 $kJ\cdot mol^{-1}$ at x_2 (min) = 0.71_1 at 318.15 K.

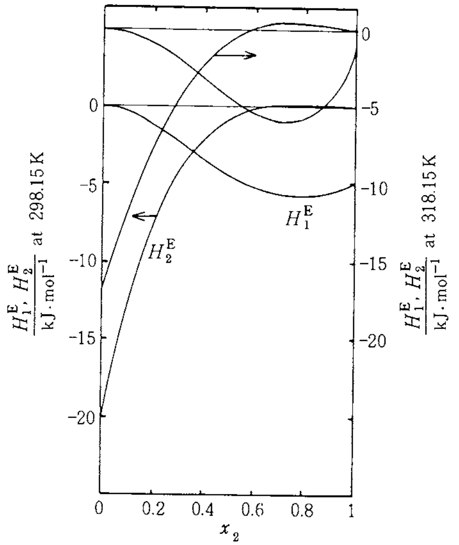

Fig. 9 Excess partial molar enthalpies of {water(1) + DMSO(2)} at 298.15 and 318.15 K calculated by Eq. (1) with the coefficients from Table 2. H_1^E (min) and H_2^E (max) are respectively -5.7_9 and 0.08 $kJ\cdot mol^{-1}$ at x_2 (min) = 0.77_3 at 298.15 K and -5.9_6 and 0.44 $kJ\cdot mol^{-1}$ at x_2 (min) = 0.72_5 at 318.15 K.

Table 3. Excess partial molar enthalpies at infinite dilution obtained from Eq. (1) or Eq. (2) with the coefficients from Table 2.

System	$\frac{T}{\mathrm{K}}$	$\frac{H_1^{\mathrm{E},\infty}(x_2 \simeq 1)}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{H_2^{\mathrm{E},\infty}(x_2 \simeq 0)}{\mathrm{kJ \cdot mol^{-1}}}$
water(1) + MMTSO(2)	298.15	−0.91	−15
	318.15	−1.4	−11
benzene(1) + MMTSO(2)	298.15	1.5	3.5
	318.15	1.6	3.5
water(1) + DMSO(2)	298.15	−4.9	−20
	318.15	−4.3	−19
benzene(1) + DMSO(2)	298.15	2.5	3.3
	318.15	2.7	3.6

in the water-rich region. The former is a quite reasonable assumption, because a DMSO molecule has ability to donate an electron to neighbouring molecule to form a chemical bond.[19] This may be the reason for the large evolution of heat in this mixture. The latter may cause the minimum in H_1^{E} (and the maximum in H_2^{E}) and consequently the point of inflection in the $H_{\mathrm{m}}^{\mathrm{E}}$ vs x curve. The charge donating ability, in other words, the proton accepting ability of the $>\mathrm{S{=}O}$ oxygen of MMTSO molecule may decrease by the substitution of a $-\mathrm{CH_2-S-CH_3}$ group for a $-\mathrm{CH_3}$ group of DMSO.

The limiting values of excess partial molar enthalpies are summarised in Table 3.

Above discussions show the importance of inspecting the concentration-dependence of partial molar quantities in mixtures, as the present authors[20,21] and others have stated.

Acknowledgments

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