

Thermodynamic Properties of Binary Mixtures Containing Sulfur Amide. 2. Excess Molar Volumes of 1,4-Dioxane + *N,N*-Dimethylmethanesulfinamide and 1,4-Dioxane + *N*-Methylmethanesulfinamide

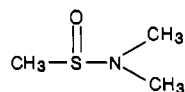
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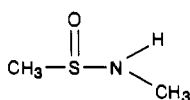
Excess molar volumes for the binary mixtures of *N*-methylmethanesulfinamide and *N,N*-dimethylmethanesulfinamide with 1,4-dioxane were calculated from experimental density data at 303.44, 313.28, 323.20, and 333.22 K over the entire composition range. The excess molar volumes are mostly positive for *N,N*-dimethylmethanesulfinamide + 1,4-dioxane mixtures at 303.44 and 313.28 K, and mostly negative at 323.20 and 333.22 K. The excess molar volumes are negative for *N*-methylmethanesulfinamide + 1,4-dioxane mixtures over the whole mole fraction range. The results are discussed in terms of the strength of the molecular interactions in the two binary mixtures.

Introduction

Previous publications (1-5) from our laboratory have described measurements of excess molar volumes, dipole moments, and IR and NMR spectroscopic quantities of sulfinamides in various solvent mixtures. Since we have used 1,4-dioxane as the main solvent in the dipole moment measurements, it was of interest to know the extent of the molecular interactions of sulfinamides with this solvent over the whole composition range. Accordingly, in this work we have extended our studies to the excess molar volumes of binary systems involving 1,4-dioxane + *N,N*-dimethylmethanesulfinamide (I) and 1,4-dioxane + *N*-methylmethanesulfinamide (II).



I, *N,N*-dimethylmethanesulfinamide



II, *N*-methylmethanesulfinamide

Experimental Section

N,N-Dimethylmethanesulfinamide was prepared from methanesulfinyl chloride and dimethylamine (6, 7), and *N*-methylmethanesulfinamide from methanesulfinyl chloride and methylamine (6, 7), both in anhydrous ether at -10 °C. Methanesulfinyl chloride was obtained by chlorination of dimethyl disulfide in acetic anhydride at -10 °C. Amides were purified by distillation and preserved over molecular sieves 4A.

1,4-Dioxane, E. Merck AG (p. a.), Darmstadt, FRG, was first refluxed for 12 h with a HCl-water mixture under nitrogen atmosphere, and then refluxed twice with sodium and distilled over sodium.

Table I. Densities (ρ) of the Pure Components at Various Temperatures

compound	$\rho/\text{g cm}^{-3}$			
	303.44 K	313.28 K	323.20 K	333.22 K
1,4-dioxane	1.02225 (1.02210) ^a	1.01157 (1.01095) ^b	1.00028 (0.99961) ^c	0.98840 (0.9882) ^d
<i>N</i> -methylmethanesulfinamide	1.14228	1.13387	1.12503	1.11588
<i>N,N</i> -dimethylmethanesulfinamide	1.06647	1.05714	1.04733	1.03733

^aReference 8 at 303.15 K. ^bReference 8 at 313.15 K. ^cReference 8 at 323.15 K. ^dReference 9 at 333.15 K.

Table II. Molar Excess Volumes V^E for *N,N*-Dimethylmethanesulfinamide + 1,4-Dioxane

x_1^a	$V^E/\text{cm}^3 \text{ mol}^{-1}$			
	303.44 K	313.28 K	323.20 K	333.22 K
0.000 00	0.0000	0.0000	0.0000	0.0000
0.113 45	0.0016	0.0091	0.0068	-0.0240
0.198 22	0.0069	0.0043	-0.0042	-0.0246
0.333 21	0.0152	0.0092	-0.0040	-0.0327
0.420 51	0.0142	0.0063	-0.0143	-0.0352
0.499 99	0.0257	0.0177	-0.0067	-0.0341
0.558 63	0.0128	0.0072	-0.0104	-0.0439
0.586 06	0.0155	0.0096	-0.0099	-0.0281
0.707 37	0.0132	0.0098	-0.0057	-0.0219
0.838 24	0.0053	0.0044	-0.0072	-0.0125
0.871 05	0.0013	0.0043	-0.0165	-0.0322
1.000 00	0.0000	0.0000	0.0000	0.0000

^a x_1 = mole fraction of *N,N*-dimethylmethanesulfinamide in binary mixture.

Densities were measured with a digital density meter DMA 40 (Anton Paar K.G., Granz, Austria) with a reproducibility within $\pm 0.0001 \text{ g cm}^{-3}$ at 303.44, 313.28, 323.20, and 333.22 K. In this technique the density (ρ) of a liquid depends on the square of the period (T) of vibration of the sample tube according to the equation

$$\rho = A(T^2 - B) \quad (1)$$

where A and B are calibration constants. Distilled water and air were used to obtain the constants.

Results and Discussion

Experimental densities of the pure compounds are given in Table I, along with those found in the literature, for each temperature in our experiments.

The experimental excess molar volumes (V^E) are given in

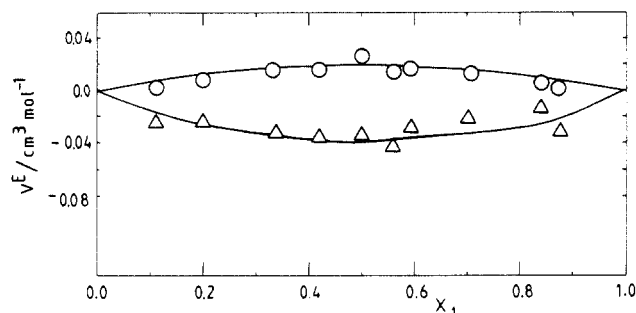


Figure 1. Molar excess volumes of *N,N*-dimethylmethanesulfonamide + 1,4-dioxane at $T = 303.44$ K (O) and 333.22 K (Δ).

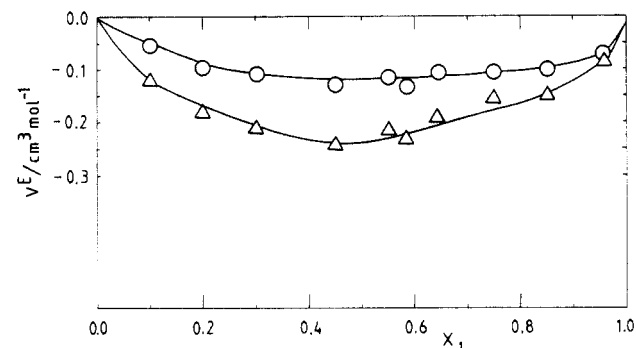


Figure 2. Molar excess volumes of *N*-methylmethanesulfonamide + 1,4-dioxane at $T = 303.44$ K (O) and 333.22 K (Δ).

Table III. Molar Excess Volumes V^E for *N*-Methylmethanesulfonamide + 1,4-Dioxane

x_1^a	$V^E/\text{cm}^3 \text{ mol}^{-1}$			
	303.44 K	313.28 K	323.20 K	333.22 K
0.0000	0.0000	0.0000	0.0000	0.0000
0.10141	-0.0549	-0.0589	-0.0768	-0.1183
0.20251	-0.0972	-0.1107	-0.1294	-0.1807
0.30007	-0.1113	-0.1317	-0.1678	-0.2126
0.44947	-0.1340	-0.1607	-0.1930	-0.2408
0.55181	-0.1177	-0.1364	-0.1731	-0.2151
0.58166	-0.1380	-0.1679	-0.1958	-0.2434
0.64500	-0.1098	-0.1296	-0.1564	-0.1913
0.75164	-0.1074	-0.1216	-0.1379	-0.1537
0.85038	-0.1042	-0.1159	-0.1361	-0.1550
0.95693	-0.0720	-0.0709	-0.0764	-0.0842
1.00000	0.0000	0.0000	0.0000	0.0000

^a x_1 = mole fraction of *N*-methylmethanesulfonamide in binary mixture.

Table II for *N,N*-dimethylmethanesulfonamide + 1,4-dioxane mixtures and in Table III for *N*-methylmethanesulfonamide + 1,4-dioxane mixtures and are plotted as a function of molar fractions of the amides in Figures 1 and 2, respectively. The experimental values were calculated from the equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (2)$$

where x is mole fraction, M molar mass, and ρ density and the indexes 1, 2, and 12 refer to amide, 1,4-dioxane, and the mixture, respectively.

To the obtained V^E values was fitted the smoothing equation

$$V^E (\text{cm}^3 \text{ mol}^{-1}) = x_1 (1 - x_1) \sum_{k=0}^n A_k (1 - 2x_1)^k \quad (3)$$

where $k = 0, 1, \dots, n$ and x_1 is the mole fraction of the amide. The parameters A_k presented in Table IV were obtained by the method of least squares.

The standard deviation (V^E) was defined by the equation

$$\sigma(V^E) = [\sum (V_{\text{obsd}}^E - V_{\text{calcd}}^E)^2 / (n - m)]^{1/2} \quad (4)$$

where n is the number of experimental points and m is the number of parameters.

The values of the excess molar volumes for *N,N*-dimethylmethanesulfonamide + 1,4-dioxane mixtures (Table II) are small, suggesting that molecular interactions between the unlike molecules are weak. That the V^E values are positive with one exception at 303.44 and 313.28 K and mostly negative at 323.20 and 333.22 K is perhaps due to the changes in dipolar association with temperature. 1,4-Dioxane has a zero dipole moment and a low dielectric permittivity, but between sulfonamide molecules the intermolecular forces should be dipolar, as the dipole moment for *N,N*-dimethylmethanesulfonamide determined in 1,4-dioxane is 3.12 D (2).

N-Methylmethanesulfonamide + 1,4-dioxane mixtures have small negative V^E values over the entire composition range at all temperatures (Table III). Unlike *N,N*-dimethylmethanesulfonamide, the *N*-methylmethanesulfonamide molecule is able to self-associate by forming hydrogen bonds between the NH proton and O atom of the amide group. A solvent like 1,4-dioxane is capable of disrupting the amide-amide hydrogen bonds by competing for one of the hydrogen-bonding sites of the amide molecule, and for that reason we chose it as the main solvent in dipole moment measurements. Furthermore, 1,4-dioxane makes a good competitive solvent, since it cannot self-associate. The proton-accepting capacity of 1,4-dioxane is well-known and exceeds that of diethyl ether (10).

The V^E values are less negative for *N*-methylmethanesulfonamide + 1,4-dioxane mixtures than for mixtures of the amide with carbon tetrachloride (1), which suggests that $\text{N} \cdots \text{H} \cdots \text{O} = \text{S}$ association is considerably reduced in 1,4-dioxane. Carbon tetrachloride is of course a weak electron acceptor (acceptor number $\text{AN} = 8.6$) (11) and can form weak charge-transfer complexes with amides, whereas 1,4-dioxane is a weak electron donor, as was mentioned earlier.

Table IV. Coefficients A_k and Standard Deviations for Representations of Excess Volumes of Component 1 + 1,4-Dioxane Systems Calculated by Eq 3 and 4

component 1	temp K	$A_0/\text{cm}^3 \text{ mol}^{-1}$	$A_1/\text{cm}^3 \text{ mol}^{-1}$	$A_2/\text{cm}^3 \text{ mol}^{-1}$	$A_3/\text{cm}^3 \text{ mol}^{-1}$	$A_4/\text{cm}^3 \text{ mol}^{-1}$	$\sigma(V^E)/\text{cm}^3 \text{ mol}^{-1}$
<i>N,N</i> -dimethylmethanesulfonamide	303.44	0.072	0.007	-0.057	-0.012	-0.065	0.003
	313.28	0.043	-0.046	-0.015	0.198	-0.052	0.004
	323.20	-0.043	-0.044	0.142	0.215	-0.192	0.005
	333.22	-0.154	-0.062	0.392	0.108	-0.928	0.006
<i>N</i> -methylmethanesulfonamide	303.44	-0.524	-0.038	0.116	-0.177	-1.045	0.007
	313.28	-0.625	-0.079	0.145	0.030	-0.967	0.010
	323.20	-0.772	-0.249	0.333	0.863	-1.335	0.008
	333.22	-0.963	-0.338	0.518	0.675	-1.930	0.011

Registry No. *N*-Methylmethanesulfinamide, 18649-17-7; *N,N*-dimethylmethanesulfinamide, 920-56-9; 1,4-dioxane, 123-91-1.

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Thermochemistry of Inorganic Solids. 5. Empirical Relations among Enthalpies of Formation of Oxides, Carbonates, Sulfates, Hydroxides, and Nitrates

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Examination of the existing data of standard enthalpies of formation of solid metal oxides, carbonates, sulfates, hydroxides, and nitrates reveals the fact that the standard enthalpies of formation of any three compounds for a particular metal oxidation state can be correlated quantitatively by the following two-parameter linear equations: for mono- and divalent compounds, $(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) = 1.36(\Delta H^\circ_{(\text{CO}_3)} - \Delta H^\circ_{(\text{O})}) - 3.2$ kcal/mol (1); for monovalent compounds, $(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})}) = 0.463(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 2.3$ kcal/mol (2), and $(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})}) = 1.02(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 56.1$ kcal/mol (4); for divalent compounds, $(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})}) = 0.318(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) + 22.6$ kcal/mol (3), and $(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})}) = 1.025(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 119.6$ kcal/mol (5), where $\Delta H^\circ_{(\text{O})}$, $\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{NO}_3)}$, and $\Delta H^\circ_{(\text{OH})}$ are the standard enthalpies of formation in kcalories per mole of the oxide, sulfate, carbonate, nitrate, and hydroxide of the metal. These equations are recast into linear equations which permit deducing ΔH_f° for monovalent and divalent metal salts from the ΔH_f° of their oxides and any of their other salts. Considering the accuracy involved in the reference compounds, for different compounds of various metals examined the maximum absolute deviation is only 3 kcal/mol.

Introduction

As part of a program to understand the bonding and the kinetic behavior of solid inorganic catalysts, we have been exploring the known thermochemistry of inorganic solids. In the course of this, we have discovered a number of empirical relations which permit us to make estimations of the enthalpies of formation of inorganic salts and their hydrates. No comparable estimation methods now exist for these substances. In

Table I. Standard Enthalpies of Formation ($\Delta H_f^\circ_{298}$) of Solid Metal Oxides, Sulfates, Carbonates, Nitrates, and Hydroxides

metal	valence state	$-\Delta H_f^\circ_{298}$, kcal/mol of metal				
		oxide	sulfate	carbonate	nitrate	hydroxide
Li	1	71.5	171.7	145.3	115.5	115.9
Na	1	49.5	165.8	135.1	111.8	101.7
K	1	43.2	171.8	137.6	118.2	101.5
Rb	1	40.5	171.6	135.8	118.3	99.9
Cs	1	41.3	172.4	136.2	120.9	99.7
Tl	1	21.4	111.4	83.7	58.3	57.1
Ag	1	3.7	85.6	60.4	29.7	
Be	2	145.7	288.0	245.0		215.7
Mg	2	143.4	307.1	261.9	189.0	221.0
Ca	2	151.8	341.0 ^a	288.5	224.3	235.7
Sr	2	141.5	346.9 ^a	291.6	233.8	229.0
Ba	2	132.3	351.3 ^a	290.7	237.1	225.8
Ra	2	125.0	351.6		237.1	
Pb	2	52.1	219.9	167.1	108.0	
Cd	2	61.7	223.1	179.4	109.1	134.0
Mn	2	92.0	254.6	213.7	137.7	166.2
Fe	2	65.0	221.9	177.0		136.0
Co	2	56.9	212.3	170.4	100.5	129.0
Ni	2	57.3	208.6		99.2	126.6
Cu	2	37.6	184.4		72.4	107.5
Zn	2	83.2	234.9	194.3	115.6	153.4

^aAn average values is taken for these compounds where more than one value is reported depending upon the structural types.

recent papers (1, 2), we have presented evidence that a quantitative relationship exists between the standard enthalpies of formation of the different valence states of solid polyvalent binary metal compounds of the formula MX_z (where X is either metal or nonmetal) and the value of z . We have also shown (3) that for solid metal oxyhalide compounds of different valence states, the standard enthalpies of formation can be related quantitatively to the corresponding halides and oxides of the same oxidation states.