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THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING SULFUR AMIDE. 1. EXCESS MOLAR VOLUMES OF CARBON TETRACHLORIDE + *N*,*N*-DIMETHYLMETHANESULFINAMIDE AND +*N*-METHYLMETHANESULFINAMIDE

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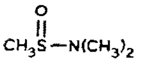
ABSTRACT

Excess molar volumes have been determined for binary mixtures of carbon tetrachloride + *N*,*N*-dimethylmethanesulfinamide and + *N*-methylmethanesulfinamide at 303.44, 313.28, 323,20 and 333.22 K. The excess molar volumes are negative for *N*,*N*-dimethylmethanesulfinamide mixture over the whole mole-fraction range and negative for *N*-methylmethanesulfinamide mixtures over the mole-fraction range 0.4–1.0 (solubility range). The results are interpreted in terms of the possibility of the components to form self-associated and charge transfer complexes.

INTRODUCTION

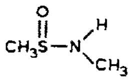
We have systematically studied the molecular interactions of organic mixtures containing sulfinamide as one component and an alcohol as the other [1,2]. Our IR and NMR spectroscopic studies show that the interactions of sulfinamides in binary or ternary solution mixtures are of the same order of magnitude as those of carboxamides [2,3]. Further, the behaviour of these amides resembles closely that of sulfoxides. Since carbon tetrachloride is the main solvent in our spectroscopic work, it was of interest to extend the studies to the thermodynamic excess quantities such as excess volumes for binary solution mixtures of sulfinamides and this solvent. Among the sulfinamides for the thermodynamic interaction study, we have chosen two aliphatic amides, *N*,*N*-dimethylmethanesulfinamide (**I**) and *N*-methylmethanesulfinamide (**II**). To our knowledge, there are no studies on



$CH_3S(=O)-N(CH_3)_2$

N,*N*–Dimethylmethanesulfinamide

(I)



N–Methylmethanesulfinamide

(II)

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the thermodynamic excess quantities for sulfinamides reported in the literature.

EXPERIMENTAL

N,*N*-Dimethylmethanesulfinamide was prepared from methanesulfinyl chloride and dimethylamine [4,5], and *N*-methylmethanesulfinamide from methanesulfinyl chloride and methylamine [4,5], both in anhydrous ether at −10°C. Methanesulfinyl chloride was obtained by chlorination of dimethyldisulfide in acetic anhydride at −10°C. Amides were purified by distillation and preserved above molecular sieves 4A.

Carbon tetrachloride (reagent for IR spectroscopy from Fluka AG) was dried and stored over Union Carbide molecular sieves 4A.

Densities were measured with a digital density meter DMA 40 (manufactured by Anton Paar K.G., Granz, Austria) with a reproducibility within ± 0.0001 g cm^{-3} at 303.44, 313.28, 323.20 and 333.22 K. The density (ρ) of the liquid is related to the square of the period (T) of vibration of the sample tube, according to the equation

$$\rho = A(T^2 - B) \tag{1}$$

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

RESULTS AND DISCUSSION

The experimental excess molar volumes (V^E) are given in Table 1 for *N*,*N*-dimethylmethanesulfinamide–carbon tetrachloride mixtures and in Table 2 for *N*-methylmethanesulfinamide—carbon tetrachloride mixtures and demonstrated in Figs. 1 and 2 at 303.44 and 333.22 K, respectively. These values were calculated from the equation

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

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

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

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

where $k = 0, 1, \ldots n$ and x_1 = mole fraction of the amide, and the parameters A_k presented in Table 3 were obtained by the method of least squares.

TABLE 1

Molar excess volumes V^E for *N,N*-dimethylmethanesulfinamide + carbon tetrachloride

x_1 [a]	V^E (cm^3 mol^{-1})			
	303.44 K	313.28 K	323.20 K	333.22 K
0.00000	0.0000	0.0000	0.0000	0.0000
0.082063	−0.1290	−0.1303	−0.1367	−0.1431
0.21494	−0.3165	−0.3230	−0.3426	−0.3673
0.29644	−0.3110	−0.3184	−0.3368	−0.3566
0.40180	−0.4811	−0.4992	−0.5283	−0.5581
0.50025	−0.5152	−0.5366	−0.5704	−0.6215
0.58752	−0.5453	−0.5679	−0.5934	−0.6298
0.65137	−0.5230	−0.5461	−0.5772	−0.6323
0.73214	−0.4704	−0.5022	−0.5598	−0.6057
0.79844	−0.3777	−0.4062	−0.4436	−0.4706
0.90005	−0.1961	−0.2085	−0.2374	−0.2492
1.00000	0.0000	0.0000	0.0000	0.0000

[a] x_1 = Mole fraction of *N,N*-dimethylmethanesulfinamide in binary mixture.

TABLE 2

Molar excess volumes V^E for *N*-methylmethanesulfinamide + carbon tetrachloride

x_1 [a]	V^E (cm^3 mol^{-1})			
	303.44 K	313.28 K	323.20 K	333.22 K
0.00000	0.0000	0.0000	0.0000	0.0000
0.42109	−0.3006	−0.3191	−0.3441	−0.3731
0.52646	−0.3959	−0.4222	−0.4475	−0.4881
0.58641	−0.4052	−0.4307	−0.4424	−0.4813
0.69429	−0.3605	−0.3830	−0.4076	−0.4533
0.81532	−0.2818	−0.3021	−0.3229	−0.3555
0.85360	−0.2384	−0.2537	−0.2799	−0.3099
0.94839	−0.0443	−0.0476	−0.0614	−0.0676
1.00000	0.0000	0.0000	0.0000	0.0000

[a] x_1 = Mole fraction of *N*-methylmethanesulfinamide in binary mixture.

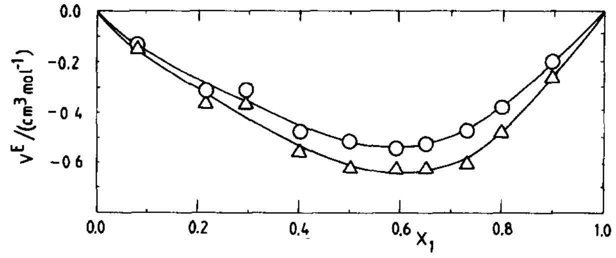

Fig. 1. Molar excess volumes of *N,N*-dimethylmethanesulfinamide + carbon tetrachloride at T = 303.44 K (○) and 333.22 K (△).

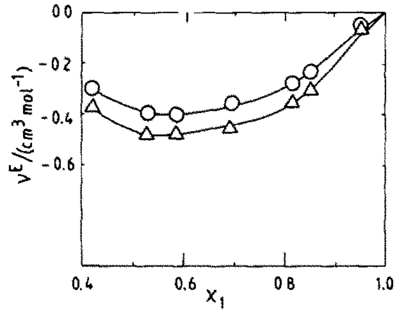

Fig. 2. Molar excess volumes of *N*-methylmethanesulfinamide + carbon tetrachloride at $T = 303.44$ K (○) and 333.22 K (△).

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

$$\sigma(V^E) = \left[\Sigma\left(V^E_{obs} - V^E_{calc}\right)^2/n - m\right]^{1/2} \tag{4}$$

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

As Table 1 shows, the V^E values are negative over the whole composition range for *N,N*-dimethylmethanesulfinamide–carbon tetrachloride mixtures at all temperatures. The magnitude of the deviation from ideality increases with temperature, as $V^E = -0.5453$ at 303.44; -0.5679 at 313.28; -0.5934 at 323.20 and -0.6298 cm^3 mol^{-1} at 333.22 K, respectively, corresponding to the mole fraction of 0.58752 of *N,N*-dimethylmethanesulfinamide. This behaviour of V^E and $(\partial V^E/\partial T)_p$ is similar to that for dimethyl sulfoxide–carbon tetrachloride mixtures [6,7]. The negative V^E values may be due to the ability of the sulfinamide group to act as an electron donor and carbon tetrachloride as an electron acceptor molecule (acceptor number AN = 8.6 for CCl_4 compared with hexane) [8] in weak charge transfer complex formation.

Interaction of *N*-methylmethanesulfinamide with carbon tetrachloride is also evident, as V^E values are negative over the whole composition range (Table 2). The V^E values are slightly less negative for *N*-methylmethanesulfinamide– than for *N,N*-dimethylmethanesulfinamide–carbon tetrachloride mixtures, however. *N*-Monosubstituted amides, as *N*-methylmethanesulfinamide, are able to self-associate by hydrogen-bonding. Furthermore, the self-association ability of *N*-monosubstituted sulfonamides has been found stronger or of the same order of magnitude than that of the corresponding carboxamides [9–11]. Generally, dissociation of self-associated species contribute an increase in excess volumes. The obtained negative excess volumes for *N*-methylmethanesulfinamide–carbon tetrachloride mixtures pointed out that the factors influencing the contraction in volume are dominant over the factors influencing the expansion in volume.

TABLE 3

Coefficients A_k and standard deviations for representations of excess volumes of component 1 + carbon tetrachloride systems by eqs. (3) and (4)

Component 1	Temperature (K)	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})	A_4 (cm^3 mol^{-1})	$\sigma(V^E)$ (cm^3 mol^{-1})
N,N-Dimethylmethane-sulfinamide	303.44	−2.084	0.994	0.266	−1.185	−0.182	0.024
	313.28	−2.162	1.107	0.149	−1.209	−0.021	0.025
	323.20	−2.273	1.201	−0.165	−1.114	0.239	0.028
	333.22	−2.441	1.375	−0.206	−1.396	0.441	0.031
N-Methylmethane-sulfinamide	303.44	−1.585	0.835	5.892	17.493	14.271	0.007
	313.28	−1.691	0.881	6.477	19.276	15.660	0.007
	323.20	−1.780	0.769	6.405	20.120	16.255	0.006
	333.22	−1.930	0.902	6.591	21.078	17.308	0.007

In addition, it is evident from the results in Tables 1 and 2 that the interaction of carbon tetrachloride with both N-methylmethanesulfinamide and N,N-dimethylmethanesulfinamide is weak and much alike.

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