Thermochimica Acta, 109 (1987) 377–382
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING SULFUR AMIDE. 3. EXCESS MOLAR VOLUMES OF BENZYL ALCOHOL + *N*,*N*-DIMETHYLMETHANESULFINAMIDE, + *N*,*N*-DIMETHYLBENZENESULFINAMIDE AND + DIMETHYL SULFOXIDE

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(Received 27 May 1986)

ABSTRACT

Excess volumes have been determined over the entire composition range for benzyl alcohol + *N*,*N*-dimethylmethanesulfinamide, + *N*,*N*-dimethylbenzenesulfinamide and + dimethyl sulfoxide at 303.06 and 323.21 K. The excess molar volumes are negative for all three systems, corresponding to the tendency of sulfinyl compounds to form hydrogen-bonded complexes with benzyl alcohol.

INTRODUCTION

There have been a number of spectroscopic, thermodynamic and other studies of binary solution mixtures containing dimethyl sulfoxide as one component. In our work we have used this dipolar solvent as a reference compound in exploring the spectroscopic and thermodynamic quantities of related sulfinamides [1–5].

In continuation of earlier work on the excess molar volumes of some nonpolar and polar liquids with sulfur amides, we report here a study of the excess molar volumes, V^E, in three sulfinyl compound + benzyl alcohol systems and our search for a possible correlation between V^E values and the tendency of sulfinyl compounds to form hydrogen-bonded complexes with benzyl alcohol.

EXPERIMENTAL

N,*N*-Dimethylmethanesulfinamide and *N*,*N*-dimethylbenzenesulfinamide were prepared from dimethylamine and methane- or benzenesulfinyl chloride, both in anhydrous ether at −10°C. Sulfinyl chlorides were obtained by chlorination of dimethyldisulfide or diphenyldisulfide in acetic anhydride at

0040-6031/87/$03.50

$-10°C$. Amides were purified by distillation and preserved above 4 Å molecular sieves [6].

Dimethyl sulfoxide (purum, Fluka AG, Buchs, Switzerland) was purified by distillation above CaH_2 and preserved over 4 Å molecular sieves.

Benzyl alcohol (puriss, p.a., Fluka AG, Buchs, Switzerland and Ega Chemie, Steinheim, BRD) was purified by distillation above CaO and preserved over 4 Å molecular sieves.

Densities were measured with a digital density meter DMA 40 (manufactured by Anton Paar K.G., Austria) with a reproducibility of ± 0.0001 g cm^{-3} at 303.06 and 323.15 K. In this method the density (ρ) of a liquid depends on the square of the period (T) of vibration of the sample tube according to

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

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

RESULTS AND DISCUSSION

The values of V_m^E are reported in Tables 1–3 for benzyl alcohol + *N*,*N*-dimethylmethanesulfinamide, + *N*,*N*-dimethylbenzenesulfinamide and + dimethyl sulfoxide, respectively, and are plotted as a function of molar fraction of the sulfinyl compound in Fig. 1. The experimental values were calculated from the equation

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

where x is mole fraction, M molar mass, ρ density and the indexes 1, 2 and 12 refer to the sulfinyl compound, benzyl alcohol and the mixture, respectively.

The smoothing equation applied to the obtained V^E values was

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

where $k = 0, 1, \ldots n$ and x_1 = mole fraction of the amide. Parameters A_0, A_1, A_2, A_3 and A_4 evaluated at 303.06 K by the method of least squares are given in Table 4 along with the standard deviations, which are defined by the equation

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

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

TABLE 1

Molar excess volume, V^E, for N,N-dimethylmethanesulfinamide + benzyl alcohol

Temperature (K)	x_1 [a]	V^E (cm^3 mol^{-1})	x_1 [a]	V^E (cm^3 mol^{-1})
303.06	0.0000	0.000	0.5969	−0.126
	0.0598	−0.088	0.6798	−0.100
	0.0985	−0.098	0.8012	−0.051
	0.2397	−0.158	0.8895	−0.001
	0.4054	−0.180	0.9483	−0.010
	0.4999	−0.160	1.0000	0.000
323.21	0.0000	0.000	0.5969	−0.168
	0.0598	−0.105	0.6798	−0.135
	0.0985	−0.118	0.8012	−0.073
	0.2397	−0.197	0.8895	−0.016
	0.4054	−0.222	0.9483	−0.001
	0.4999	−0.214	1.0000	0.000

[a] x_1 = Mole fraction of N,N-dimethylmethanesulfinamide in benzyl alcohol.

Alcohols are known to be associated through hydrogen bonding, and the intermolecular forces between N,N-dimethyl-substituted amide molecules or dimethyl sulfoxide molecules should be dipolar in nature [7,8]. Mixing of a sulfinyl compound with an alcohol would change the hydrogen bonding in alcohol and the dipolar interaction in the sulfinyl compound, and either or both of these changes could effect the volume changes in the mixtures. The negative excess volumes observed in the present study suggest that here the dominant factor is hydrogen bond formation between unlike molecules. The

TABLE 2

Molar excess volume, V^E, for N,N-dimethylbenzenesulfinamide + benzyl alcohol

Temperature (K)	x_1 [a]	V^E (cm^3 mol^{-1})	x_1 [a]	V^E (cm^3 mol^{-1})
303.15	0.0000	0.000	0.4892	−0.164
	0.0666	−0.056	0.5987	−0.141
	0.1254	−0.075	0.7002	−0.112
	0.2139	−0.121	0.8001	−0.083
	0.3046	−0.150	0.9022	−0.043
	0.3835	−0.171	1.0000	0.000
323.15	0.0000	0.000	0.4892	−0.163
	0.0666	−0.056	0.5987	−0.141
	0.1254	−0.082	0.7002	−0.114
	0.2139	−0.125	0.8001	−0.091
	0.3046	−0.152	0.9022	−0.047
	0.3835	−0.176	1.0000	0.000

[a] x_1 = Mole fraction of N,N-dimethylbenzenesulfinamide in benzyl alcohol.

TABLE 3

Molar excess volume, V^E, for dimethyl sulfoxide + benzyl alcohol

Temperature (K)	x_1 [a]	V^E ($cm^3\ mol^{-1}$)	x_1 [a]	V^E ($cm^3\ mol^{-1}$)
303.15	0.0000	0.000	0.5540	−0.257
	0.0917	−0.157	0.6682	−0.201
	0.2157	−0.253	0.7648	−0.154
	0.3248	−0.297	0.8936	−0.094
	0.3981	−0.294	1.0000	0.000
	0.5221	−0.268		
323.15	0.0000	0.000	0.5540	−0.308
	0.0917	−0.172	0.6682	−0.245
	0.2157	−0.316	0.7648	−0.182
	0.3248	−0.356	0.8936	−0.110
	0.3981	−0.354	1.0000	0.000
	0.5221	−0.320		

[a] x_1 = Mole fraction of dimethylsulfoxide in benzyl alcohol.

formation of hydrogen-bonded complexes could cause the packing implied by negative excess volumes; for the deviations from the ideal behaviour follow the electron donor ability of the sulfinyl compounds towards benzyl alcohol [9]: dimethyl sulfoxide > *N*,*N*-dimethylmethanesulfinamide > *N*,*N*-dimethylbenzenesulfinamide. The asymmetry of the volume contractions may be indicative of structural effects operating in addition to the specific interactions between unlike molecules.

Studies reported in the literature show the V^E values for 1-methyl-2-pyrrolidinone–alcohol systems to vary from slightly positive to clearly negative, depending on the structure of the alcohol: the contribution in the case of

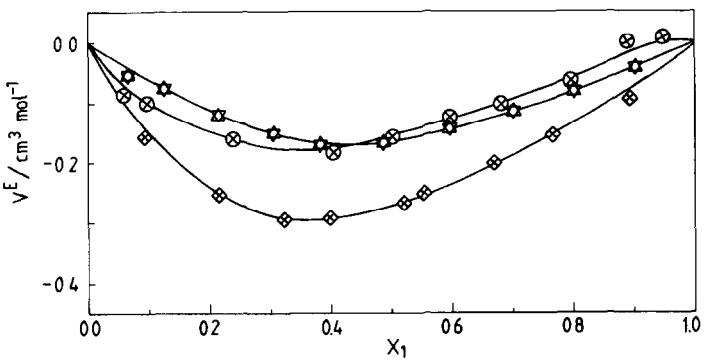

Fig. 1. Molar excess volumes of benzyl alcohol and *N*,*N*-dimethylbenzenesulfinamide (☆), *N*,*N*-dimethylmethanesulfinamide (⊗) and dimethyl sulfoxide (⊗) at 303.06 K as a function of molar fraction of the sulfinyl compound.

TABLE 4

Values of least-squares parameters (A_k) and standard deviations (σ) for three benzyl alcohol–sulfinyl compound systems obtained by fitting eqns. (3) and (4) to the observed values

Compound	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	303.06	−0.640	−0.375	0.121	−0.576	−0.101	0.008
	323.15	−0.835	−0.426	0.291	−0.571	−0.407	0.008
N,N-Dimethylbenzene-sulfinamide	303.06	−0.658	−0.251	0.277	0.162	−0.387	0.005
	323.15	−0.656	−0.264	0.137	0.206	−0.284	0.005
Dimethyl sulfoxide	303.06	−1.100	−0.648	−0.031	0.207	−0.737	0.003
	323.15	−1.318	−0.819	−0.288	0.361	−0.265	0.004

1-octanol is positive and partly positive values are found in the cases of 1-hexanol and 1-heptanol systems [10]. The positive contribution arises at least in part from disruption of the alcohol structure with breaking of hydrogen bonds by 1-methyl-2-pyrrolidinone, which has a relatively strong hydrogen bond formation ability. By contrast the V^E values are negative over the whole composition range for systems of 1-methyl-2-pyrrolidinone and methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol systems, and the present negative results for sulfinyl compound–benzyl alcohol systems are comparable to these. The hydrogen bond formation ability of *N,N*-dimethylmethanesulfinamide is of the same order of magnitude as that of 1-methyl-2-pyrrolidinone, although a little lower [1,2,11]. Dimethyl sulfoxide is the strongest base amongst the compounds dimethyl sulfoxide, 1-methyl-2-pyrrolidinone, *N,N*-dimethylmethanesulfinamide and *N,N*-dimethylbenzenesulfinamide, and the largest negative V^E values are found for the dimethyl sulfoxide–benzyl alcohol system.

In addition, it is evident from the results in Tables 1–3 that interaction of benzyl alcohol with these sulfinyl compounds is weak and fairly similar, which supports the findings of our near-IR spectroscopy study [9].

ACKNOWLEDGEMENT

Financial support from the Emil Aaltonen and Magnus Ehrnrooth Foundations is gratefully acknowledged.

REFERENCES

1 P. Ruostesuo and J. Karjalainen, Finn. Chem. Lett., (1979) 210.
2 P. Ruostesuo and J. Karjalainen, Acta Chem. Scand., Ser. A, 33 (1979) 765.
3 J. Karjalainen and P. Ruostesuo, Acta Chem. Scand., Ser. A, 34 (1980) 573.
4 P. Ruostesuo and T. Mattila, Thermochim. Acta, 104 (1986) 153.
5 P. Ruostesuo and T. Mattila, J. Chem. Eng. Data, (1986), in the press.
6 P. Ruostesuo, Acta Univ. Oulu A, 66 (1978) Chem. 6.
7 R.H. Fiqueroa, E. Roig and H.H. Szmant, Spectrochim. Acta, 22 (1966) 587.
8 F. Takahashi and N.C. Li, J. Phys. Chem., 68 (1964) 2136.
9 P. Ruostesuo and S. Kurkisuo, to be published.
10 A.M. Awward, E.I. Allos and F.I. Kanbour, J. Chem. Thermodyn., 17 (1985) 635.
11 M. Jarva, Acta Univ. Oul. A, 64 (1978) Chem. 5.