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THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING SULFUR AMIDE. PART 4. EXCESS MOLAR VOLUMES OF *N*-METHYLBENZENESULFONAMIDE + VARIOUS SOLVENTS

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ABSTRACT

Excess molar volumes have been determined over the entire composition range for *N*-methylbenzenesulfonamide + 1,2-dichloroethane, *N*-methylbenzenesulfonamide + benzyl alcohol, *N*-methylbenzenesulfonamide + 2-propanol, *N*-methylbenzenesulfonamide + dimethyl sulfoxide, *N*-methylbenzenesulfonamide + 1,4-dioxane and *N*-methylbenzenesulfonamide + acetone at 303.15 and 323.15 K. The excess molar volumes are negative for all the systems. The results have been discussed comparing the volume behavior of the sulfonamide in various solvent mixtures with the IR and NMR spectroscopic results of the studied and related compounds.

INTRODUCTION

A number of antibiotic drugs have been found among the sulfonamide derivatives, and because of this and for other reasons, much attention has been given to the structure and properties of sulfonamides [1]. Among the methods of investigation, spectroscopic (IR and NMR) and thermodynamic methods have yielded plenty of information about the interaction properties of sulfur amides [2–6].

The complex formation of sulfonamides has been found to be weak, while their polar properties are relatively high for this kind of amide. The *N*-methyl substituent increases the polarity of carboxamides and sulfonamides [7,8]. The effect of the *N*-methyl substituent is weaker in the aromatic sulfonamides than in the carboxamides. Furthermore, the dielectric permittivities of *N*-monosubstituted carboxamides are high, being significantly higher than those of *N*,*N*-disubstituted analogs [9–11]. At the same time, both *N*-monosubstituted and *N*,*N*-disubstituted sulfonamides are characterized by high dielectric permittivities, with somewhat greater values for the *N*-monosubstituted amides [9]. The high dielectric permittivities of *N*-monosubstituted carboxamides have been ascribed to the formation of

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long N–H···O=C hydrogen-bonded chains [11,12], whose existence is supported by spectroscopic studies [13,14]. *N*-monosubstituted sulfonamides, in turn, appear to self-associate to cyclic polymers [15,16] and the high dielectric permittivities have been related mainly to the large dipole moments [9].

In our earlier works we have studied the excess molar volumes of *N*-methylmethanesulfinamide, *N*,*N*-dimethylmethanesulfinamide, *N*,*N*-dimethylbenzenesulfinamide and dimethyl sulfoxide + carbon tetrachloride, + 1,4-dioxane or + benzyl alcohol mixtures [5,6,17]. These excess molar volumes were negative. In this study we report the excess molar volumes for *N*-methylbenzenesulfonamide + 1,2-dichloroethane, *N*-methylbenzenesulfonamide + 2-propanol, *N*-methylbenzenesulfonamide + benzyl alcohol, *N*-methylbenzenesulfonamide + dimethyl sulfoxide, *N*-methylbenzenesulfonamide + 1,4-dioxane and *N*-methylbenzenesulfonamide + acetone mixtures to obtain more information about sulfonamides containing an NH group where there is a possibility of interaction between both like and unlike molecules in binary sulfonamide–solvent mixtures.

EXPERIMENTAL

N-methylbenzenesulfonamide was prepared from benzenesulfonyl chloride and methylamine in anhydrous ether at −10 °C. The amide was purified by distillation and preserved above molecular sieves 4A [18].

1,2-Dichloroethane (spectroscopy, Merck, Darmstadt, F.R.G.) was dried for several months above molecular sieves 4A.

1,4-Dioxane (pro analys, Merck, Darmstadt, F.R.G.) was refluxed for 12 h with an HCl–water mixture under a nitrogen atmosphere. It was then refluxed twice with sodium, distilled above sodium and preserved above molecular sieves 4A [19].

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

2-Propanol (reinst. Merck, Darmstadt, F.R.G.) was refluxed above CaO for several hours, distilled and preserved above molecular sieves 4A [20].

Dimethyl sulfoxide (purum, Fluka AG, Buchs, Switzerland) was purified by distillation above CaH_2 and preserved above molecular sieves 4A [21].

Acetone (p.a. Merck AG, Darmstadt, F.R.G.) was first refluxed with $KMnO_4$. Then Na_2CO_3 was added, and after 2 h the solution was filtered and distilled, after which it was preserved above molecular sieves 4A [20].

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 303.15 and 323.15 K. The density ρ of a liquid depends on the square of the period of vibration T of the sample tube by the equation

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

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

RESULTS AND DISCUSSION

The values of $V_{\mathrm{m}}^{\mathrm{E}}$ are reported in Tables 1–6 for N-methylbenzenesulfonamide + 1,2-dichloroethane, N-methylbenzenesulfonamide + benzyl alcohol, N-methylbenzenesulfonamide + 2-propanol, N-methylbenzenesulfonamide + dimethyl sulfoxide, N-methylbenzenesulfonamide + 1,4-dioxane and N-methylbenzenesulfonamide + acetone, respectively. These experimental values were calculated from the equation

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

where x is mole fraction, M molar mass and ρ density, and the subscripts 1, 2 and 12 refer to N-methylbenzenesulfonamide, the solvent and the mixture, respectively.

The V^{E} values obtained were fitted to the smoothing equation

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

where $k = 0,1,\ldots,n$ and x_1 = mole fraction of the amide. The parameters A_k $(k = 0,1,\ldots,6)$ evaluated at 303.15 and 323.15 K by the method of least-squares are given in Table 7 together with the standard deviations, which are defined by

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

TABLE 1

Experimental excess volumes V^{E} for N-methylbenzenesulfonamide + 1,2-dichloroethane

x_1 [a]	V^{E} (cm^3 mol^{-1})	
	T = 303.15 K	T = 323.15 K
0.0000	0.0000	0.0000
0.0952	−0.1797	−0.2373
0.2024	−0.2767	−0.3829
0.2914	−0.3286	−0.4362
0.3920	−0.3353	−0.4627
0.4866	−0.3329	−0.4396
0.5930	−0.2937	−0.3828
0.6820	−0.2384	−0.3215
0.7910	−0.1640	−0.2254
0.8764	−0.1032	−0.1280
1.0000	0.0000	0.0000

[a] x_1 = mole fraction of N-methylbenzenesulfonamide.

TABLE 2

Experimental excess molar volumes V^E for *N*-methylbenzenesulfonamide + benzyl alcohol

x_1 [a]	V^E ($cm^3\ mol^{-1}$)	
	$T = 303.15$ K	$T = 323.15$ K
0.0000	0.0000	0.0000
0.1113	−0.1137	−0.1165
0.1976	−0.1780	−0.1779
0.2665	−0.2167	−0.2107
0.3644	−0.2335	−0.2316
0.4325	−0.2335	−0.2333
0.5084	−0.2217	−0.2223
0.5446	−0.2124	−0.2237
0.6569	−0.1861	−0.1862
0.8147	−0.0999	−0.1068
0.8922	−0.0618	−0.0772
1.0000	0.0000	0.0000

[a] x_1 = mole fraction of *N*-methylbenzenesulfonamide.

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

Tables 1–6 and Figs. 1 and 2 show that the V^E values are negative for all the *N*-methylbenzenesulfonamide solvent mixtures studied over the entire composition range at both temperatures. The deviations from ideality follow the order: benzyl alcohol < 1,2-dichloroethane ~ dimethyl sulfoxide < 1,4-dioxane < 2-propanol < acetone. The order is the same as found earlier for the same solvent + 2-pyrrolidinone mixtures [22].

TABLE 3

Experimental excess volumes V^E for *N*-methylbenzenesulfonamide + 2-propanol

x_1 [a]	V^E ($cm^3\ mol^{-1}$)	
	$T = 303.15$ K	$T = 323.15$ K
0.0000	0.0000	0.0000
0.0475	−0.2602	−0.2840
0.1101	−0.5033	−0.5600
0.2027	−0.7801	−0.8513
0.3071	−0.9669	−1.0536
0.3976	−1.0156	−1.1103
0.5124	−0.9660	−1.0447
0.6094	−0.8678	−0.9310
0.7047	−0.7371	−0.7921
0.8064	−0.5000	−0.5365
0.8967	−0.3065	−0.3249
1.0000	0.0000	0.0000

[a] x_1 = mole fraction of *N*-methylbenzenesulfonamide.

TABLE 4

Experimental excess volumes V^E for N-methylbenzenesulfonamide + dimethyl sulfoxide

x_1 [a]	V^E (cm^3 mol^{-1})	
	$T = 303.15$ K	$T = 323.15$ K
0.0000	0.0000	0.0000
0.1048	−0.0688	−0.0888
0.1914	−0.1586	−0.1828
0.2225	−0.1789	−0.2029
0.2990	−0.2631	−0.2937
0.4235	−0.3641	−0.3961
0.4991	−0.4154	−0.4500
0.5850	−0.4653	−0.4877
0.6672	−0.4753	−0.4945
0.7710	−0.4554	−0.4680
0.8331	−0.4020	−0.4109
0.8859	−0.3610	−0.3620
0.9450	−0.2817	−0.2754
1.0000	0.0000	0.0000

[a] x_1 = mole fraction of N-methylbenzenesulfonamide.

TABLE 5

Experimental excess volumes V^E for N-methylbenzenesulfonamide + 1,4-dioxane

x_1 [a]	V^E (cm^3 mol^{-1})	
	$T = 303.15$ K	$T = 323.15$ K
0.0000	0.0000	0.0000
0.0939	−0.3084	−0.3771
0.1960	−0.5564	−0.6671
0.2884	−0.7032	−0.8407
0.3833	−0.7800	−0.9318
0.4861	−0.7893	−0.9306
0.5839	−0.7014	−0.8341
0.6812	−0.5894	−0.6955
0.7901	−0.4105	−0.4818
0.8890	−0.2148	−0.2591
1.0000	0.0000	0.0000

[a] x_1 = mole fraction of N-methylbenzenesulfonamide.

In addition, the excess volumes of *N*-methylbenzenesulfonamide + 1,2-dichloromethane mixtures are of the same order of magnitude as obtained previously for *N*-methylmethanesulfinamide + carbon tetrachloride mixtures [5]. Both of these small negative deviations from ideality may be due to charge transfer complex formation between the oxygen atoms of the amide group and the halogenated solvent, where the amide acts as an electron donor and 1,2-dichloroethane as an electron acceptor molecule. Interstitial

TABLE 6

Experimental excess volumes V^E for *N*-methylbenzenesulfonamide + acetone

x_1 [a]	V^E (cm^3 mol^{-1})	
	$T = 303.15$ K	$T = 323.15$ K
0.0000	0.0000	0.0000
0.0487	−0.4994	−0.5962
0.0960	−0.9143	−1.0992
0.1977	−1.5546	−1.8422
0.2715	−1.7473	−2.0679
0.3540	−1.7674	−2.0774
0.4393	−1.7655	−2.0650
0.5607	−1.5877	−1.8404
0.6116	−1.4876	−1.7196
0.6949	−1.3060	−1.4990
0.7485	−1.0422	−1.1948
0.8462	−0.5771	−0.6606
0.9117	−0.4281	−0.4736
1.0000	0.0000	0.0000

[a] x_1 = mole fraction of *N*-methylbenzenesulfonamide.

accommodation of haloalkane molecules in hydrogen-bonded *N*-methylbenzenesulfonamide aggregates is also possible.

In connection with a study of the association of an amide containing an NH group with a proton acceptor, it becomes important to determine the extent to which the self-association of the former interferes with the formation of hydrogen bonds with unlike molecules. The presence of an NH group in *N*-methylbenzenesulfonamide appears to be responsible for SO_2-NH · · · O-like association species in 1,4-dioxane + amide, acetone + amide and dimethyl sulfoxide + amide mixtures.

It is known that the self-association of a sulfonamide containing an NH group is strong [15]. It is further known that alcohols associate by hydrogen bonding giving variable degrees of polymerization. *N*-methylbenzenesulfonamide may reasonably be expected to disturb the alcohol structure and cause the breaking of hydrogen bonds. Weak hydrogen bond interaction between the oxygen atom of the sulfonyl group and the proton donor is also evident, in agreement with the results for *N*-methylbenzenesulfonamide + benzyl alcohol and *N*-methylbenzenesulfonamide + 2-propanol mixtures.

Dimethyl sulfoxide acts as an aprotic solvent with high dipole moment (~ 4.0 D) and high dielectric permittivity (46.02). The relatively strong self-association of dimethyl sulfoxide has also been found by other methods. The dissociation of self-associated species contributes to an increase in excess volume. The results for dimethyl sulfoxide + *N*-methylbenzenesulfonamide mixtures in Table 4 show that the structure-breaking effects in dimethyl sulfoxide + *N*-methylsulfonamide mixtures are remarkable com-

TABLE 7

Coefficients A_k and standard deviations for representations of excess volumes of *N*-methylbenzenesulfonamide + component(2) systems using eqns. (3) and (4)

Component (2)	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 ($cm^3 mol^{-1}$)	A_5 ($cm^3 mol^{-1}$)	A_6 ($cm^3 mol^{-1}$)	$\sigma(V^E)$ ($cm^3 mol^{-1}$)
1,2-Dichloroethane	303.15	−1.313	−0.541	0.063	−0.239	−0.564	–	–	0.004
	323.15	−1.737	−0.765	−0.306	−0.320	−0.036	–	–	0.004
Benzyl alcohol	303.15	−0.888	−0.318	−0.696	−0.329	2.838	0.514	−2.816	0.002
	323.15	−0.909	−0.247	−0.255	−0.642	1.290	1.058	−1.782	0.003
2-Propanol	303.15	−3.938	−1.350	−0.328	0.141	−0.249	–	–	0.011
	323.15	−4.265	−1.560	−0.370	0.159	−0.303	–	–	0.012
Dimethylsulfoxide	303.15	−1.659	1.333	−1.221	−0.956	4.356	3.087	−6.421	0.007
	323.15	−1.785	1.206	−1.033	−0.544	3.754	2.408	−5.860	0.007
1,4-Dioxane	303.15	−3.097	−0.963	0.326	0.111	–	–	–	0.005
	323.15	−3.668	−1.199	0.294	0.136	–	–	–	0.004
Acetone	303.15	−6.671	−1.903	−5.763	−9.852	16.482	11.533	−15.587	0.026
	323.15	−7.777	−2.549	−6.475	−10.925	17.225	12.471	−15.851	0.029

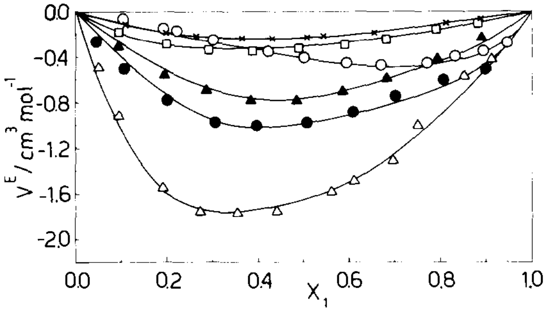

Fig. 1. Excess molar volumes V^E at 303.15 K for *N*-methylbenzenesulfonamide + 1,2-dichloroethane (□), *N*-methylbenzenesulfonamide + benzyl alcohol (×), *N*-methylbenzenesulfonamide + 2-propanol (●), *N*-methylbenzenesulfonamide + dimethyl sulfoxide (○), *N*-methylbenzenesulfonamide + 1,4-dioxane (▲) and *N*-methylbenzenesulfonamide + acetone (△).

pared with the structure-making effects by hydrogen bonding or by other association possibilities, since the excess volumes are only slightly negative. The result is understable, as both components of the mixtures are strongly self-associated.

For dimethyl sulfoxide + *N*-methylbenzenesulfonamide mixtures the deviation from ideality is clearly smaller than for corresponding acetone mixtures. This may be caused by the polarity difference between dimethyl sulfoxide and acetone ($\epsilon = 20.22$; $\mu = 2.76$ D [23]). The polarity of sulfonamides is of the same order of magnitude as that of dimethyl sulfoxide [8]. Further inspection of the results shows that the V^E values for 1,4-dioxane + *N*-methylbenzenesulfonamide mixtures are very similar to those obtained by Sacco and Jannelli [24] for 1,4-dioxane + sulfolane mixtures. In addition, the negative deviation from ideality is greater for acetone than for 1,4-dioxane mixtures. This order is the basicity order between acetone and 1,4-dioxane, as equilibrium constants are 4.8 dm^3 mol^{-1} for 1,4-dioxane–phenol com-

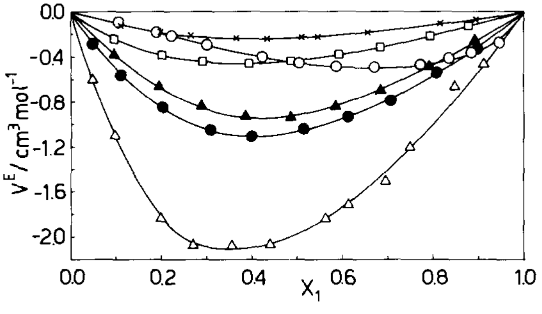

Fig. 2. Excess molar volumes V^E at 323.15 K for *N*-methylbenzenesulfonamide + 1,2-dichloroethane (□), *N*-methylbenzenesulfonamide + benzyl alcohol (×), *N*-methylbenzenesulfonamide + 2-propanol (●), *N*-methylbenzenesulfonamide + dimethyl sulfoxide (○), *N*-methylbenzenesulfonamide + 1,4-dioxane (▲) and *N*-methylbenzenesulfonamide + acetone (△).

plexes and 13.5 dm^3 mol^{-1} for acetone–phenol complexes at 298.15 K in carbon tetrachloride.

Finally, a comparison between the V^E values for various mixtures shows that the structure-making effects, such as complex formation, between the unlike components, exceed the structure-breaking effects, although the basicity of the oxygen atom of a sulfonamide group is relatively low according to IR spectroscopic studies.

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