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Excess Enthalpies of Binary Solvent Mixtures of *N*,*N*-Diethylmethanesulfonamide with Aliphatic Alcohols

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The molar excess enthalpies of binary solvent mixtures of *N*,*N*-diethylmethanesulfonamide with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol were measured with a flow microcalorimeter at 313.15 K. The excess enthalpies were positive and large in magnitude and increased with the length of the alkyl chain of the alcohol. The partial molar excess enthalpies were evaluated as well. An interpretation of the intermolecular interactions contributing to the enthalpies is made on the basis of the results.

Introduction

The ability of compounds to form hydrogen bonds has a marked effect on the enthalpies of mixing. In addition, interactions of dipolar origin affect the excess enthalpies. In our earlier studies (*1*, *2*) we have measured enthalpies of mixing of *N*,*N*-dimethyl- and *N*-methylacetamide with aliphatic alcohols at 313.15 K. This temperature was chosen for the measurements because some of the compounds have relatively high melting points (e.g., the melting point of *N*-methylacetamide is 303 K) and are relatively viscous at lower temperatures. The molecules of these carboxamides are dipolar and possess relatively good proton-accepting abilities (*3*, *4*). The sulfonyl group of the corresponding sulfonamides, *N*,*N*-dimethyl- and *N*-methylmethanesulfonamide can also function as a proton acceptor, but its ability to form hydrogen bonds with typical proton donors is considerably weaker than that of the carboxamides (*3*-*7*). On the other hand, the dipole moments of the methanesulfonamides are greater than those of the acetamides (*8*, *9*), and while N,N-disubstituted carboxamides possess considerably smaller dielectric permittivities than the N-monosubstituted amides, both N,N-di- and N-monosubstituted sulfonamides are characterized by high dielectric permittivities (*10*-*12*). To see how these features are expressed in the enthalpies of mixing of the sulfonamides with alcohols, we have measured the molar excess enthalpies for binary mixtures of *N*,*N*-diethylmethanesulfonamide (DEMSA), $CH_3SO_2N(C_2H_5)_2$, with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 313.15 K (the same temperature as in the previous studies). This amide was chosen rather than the dimethyl-substituted analogue because the latter has a high melting point (323 K).

Experimental Section

Materials. The alcohols were the same as in the previous study (*1*). *N*,*N*-Diethylmethanesulfonamide was prepared from methanesulfonyl chloride and diethylamine in anhydrous ether solution. The product was purified by distillations under reduced pressure and was confirmed pure by its refractive index (1.4467, lit. (*13*) 1.4468 at 298.15 K) and spectra recorded on a Kratos MS 80 RF Autoconsole mass spectrometer with capillary gas chromatographic sample inlet system.

Measurements. The excess enthalpies were determined by using a flow microcalorimeter (LKB-2107, LKB-Produkter AB). Two infusion pumps (Perfusor, B. Braun Melsungen AG) and gas-tight syringes (Hamilton Bonaduz AG) were used to pump the liquids through the calorimeter. The pumps and syringes were placed in a thermostated glovebox. Flow rates were determined for each pump and syringe with distilled water, alcohol, or amide. The recorder response was calibrated with a built-in electrical heater. Different calibration constants were determined according to the flow rate, the composition of the mixture, and the amplification needed. The error in the excess enthalpies is estimated to be less than 1-2% over most of the mole fraction range.

Results and Discussion

The molar excess enthalpies for the binary mixtures are reported in Table I and are also presented graphically as functions of x, the mole fraction of the amide, in Figure 1. To each set of experimental values we fitted the equation

$$H^E_m/(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \tag{1}$$

Coefficients A_i of these fitting equations together with the standard deviations $\sigma(H^E_m)$ of the fits are reported in Table II. Coefficients A_i were further used in evaluation of the partial molar excess enthalpies for the alcohols (H^E_1) and the amide (H^E_2) from the equations

$$H^E_1 = H^E_m - x\left(\frac{\partial H^E_m}{\partial x}\right)_{p,T} \tag{2}$$

$$H^E_2 = H^E_m + (1-x)\left(\frac{\partial H^E_m}{\partial x}\right)_{p,T} \tag{3}$$

The curves of H^E_1 and H^E_2 as functions of x are plotted in Figure 2.

The values of H^E_m, H^E_1, and H^E_2 are positive over the whole composition range for all the DEMSA-alcohol mixtures studied. In all $H^E_m(x)$ curves the maximum is large in magnitude and lies at about $x = 0.5$. For the primary alcohols it increases with

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Table I. Molar Excess Enthalpies H^E_m of Binary Mixtures of DEMSA with Aliphatic Alcohols at 313.15 K

x^a	H^E_m/J mol^{-1}	x^a	H^E_m/J mol^{-1}	x^a	H^E_m/J mol^{-1}
		Methanol			
0.0562	386	0.2825	1302	0.5948	1386
0.0682	461	0.3717	1421	0.6659	1257
0.1062	666	0.4235	1478	0.7480	1035
0.1292	792	0.4454	1482	0.7990	890
0.2286	1133	0.5447	1437		
		Ethanol			
0.0789	733	0.3617	1915	0.7414	1468
0.0953	842	0.4598	1975	0.8103	1142
0.1460	1144	0.5360	1955	0.8511	965
0.1759	1336	0.6325	1770		
0.2989	1769	0.6787	1672		
		1-Propanol			
0.0988	1053	0.4204	2293	0.7300	1743
0.1188	1185	0.5214	2263	0.7858	1449
0.1795	1612	0.5750	2197	0.8454	1102
0.2145	1758	0.5966	2172	0.8798	874
0.3531	2172	0.6878	1872		
		2-Propanol			
0.1010	1205	0.4263	2553	0.7348	1861
0.1214	1354	0.5275	2517	0.8486	1185
0.1832	1766	0.5810	2383	0.8824	987
0.2187	1937	0.6025	2334		
0.3587	2457	0.6930	1993		
		1-Butanol			
0.1183	1291	0.4004	2414	0.7679	1638
0.1416	1446	0.4802	2414	0.8699	1024
0.2112	1909	0.5713	2339	0.8813	976
0.2505	2069	0.6491	2134		
0.3330	2344	0.7294	1796		
		2-Methyl-2-propanol			
0.0927	1065	0.3409	2403	0.7363	1725
0.1220	1323	0.4089	2500	0.7741	1490
0.1459	1452	0.4789	2527	0.8739	931
0.2171	1907	0.5799	2331	0.9027	722
0.2571	2076	0.6316	2140		

[a] x is the mole fraction of DEMSA.

the length of the alkyl chain, from 1500 J mol^{-1} for methanol to 2400 J mol^{-1} for 1-butanol. The values for 2-propanol and 2-methyl-2-propanol are greater than those for the primary alcohols. Experimental values with which to compare our results were not found in the literature.

The $H^E_m(x)$ plots may be interpreted in terms of the changes that occur in intermolecular interactions when the components are mixed. Generally, positive contributions to the excess enthalpies are due to loosening of solute–solute interactions and negative contribution arise when the solute interacts with the solvent.

The high viscosities, high dielectric permittivities, and large dipole moments of sulfonamides suggest that the molecules are associated in the pure state, mainly by dipole–dipole interactions (*10*, *13*). The molecules of pure alcohols, in turn, are extensively self-associated through hydrogen bonding. The enthalpies of association for the present alcohols vary only slightly with the length and branching of the alkyl group; the mean value is −25 ± 2 kJ mol^{-1} (*14*).

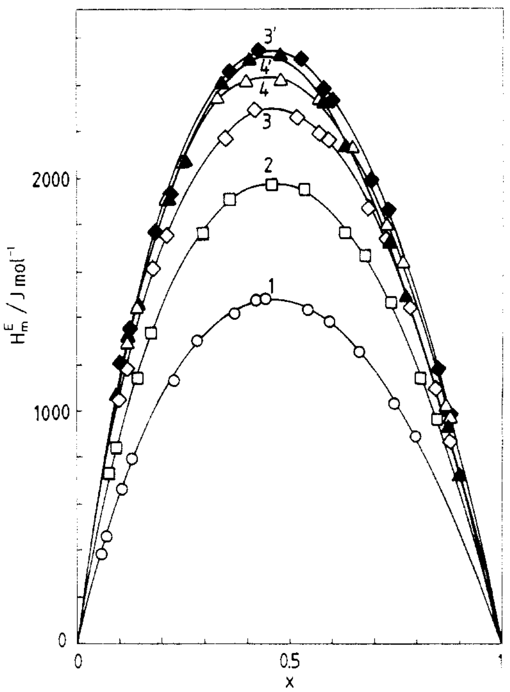

Figure 1. Molar excess enthalpies H^E_m for the mixtures of *N*,*N*-diethylmethanesulfonamide with aliphatic alcohols vs. the mole fraction x of DEMSA: 1, methanol; 2, ethanol; 3, 1-propanol; 3', 2-propanol; 4, 1-butanol; 4', 2-methyl-2-propanol.

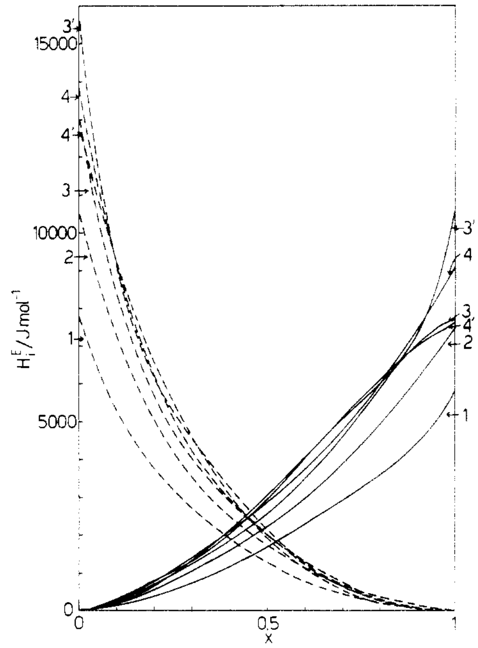

Figure 2. Partial molar excess enthalpies for the mixtures of DEMSA with aliphatic alcohols: alcohols H^E_1 solid lines; DEMSA H^E_2 dashed lines. The symbols of the alcohols are the same as in Figure 1.

When a sulfonamide or an alcohol is mixed with an inert solvent, the main contributions are due to breakup of interactions between the amide molecules on one hand and the al-

Table II. Coefficients A_i of Eq 1 and the Standard Deviations $\sigma(H^E_m)$

	DEMSA +					
	methanol	ethanol	1-propanol	2-propanol	1-butanol	2-methyl-2-propanol
A_0	5892	7881	9153	10131	9692	9905
A_1	871.3	1029	1079	1618	1691	2269
A_2	216.5	1126	1165	−163.2	1729	293.2
A_3	132.0	520.2	1694	905.2	669.8	406.1
A_4	702.4		89.8	3132		
$\sigma(H^E_m)$/J mol^{-1}	9	14	16	19	16	24

cohol molecules on the other. Owing to insufficient solubility of the compounds the $H^E_m(x)$ curves for mixtures of DEMSA with inert solvents like hydrocarbons are not available. The enthalpies of mixing of the present alcohols with a *n*-alkane change relatively little with the length of the alkyl chain of the alcohol (*15*–*17*). For example, the maximum in the $H^E_m(x)$ curve for mixtures of methanol, ethanol, 1-propanol, and 1-butanol with *n*-hexane at 318.15 K is at about 0.3–0.4 mole fraction of the alcohol and in magnitude is about 760, 830, 910, and 850 J mol^{-1}, respectively (*15*). The values for the mixtures of 2-propanol and 2-methyl-2-propanol are greater than those for the corresponding primary alcohols (*18*–*21*).

The large positive excess enthalpies for the DEMSA–alcohol mixtures studied indicate that the breakup of interactions between like molecules is giving rise to the predominant contributions in these mixtures. However, the excess enthalpies show a marked decrease on going from the higher alcohols to methanol: H^E_m(max) is about 2300–2500 J mol^{-1} for the higher alcohols, 2000 J mol^{-1} for ethanol, and 1500 J mol^{-1} for methanol (cf. the smaller differences for the alcohol–inert solvent systems mentioned above). Furthermore, the values of H^E_2 at small x and of H^E_1 at small $1 - x$ are smaller for the DEMSA–methanol system than for the mixtures of DEMSA with the other alcohols. A possible explanation of the differences between the alcohols presents itself when we recall that the molecules of DEMSA possess some, although slight, proton-accepting ability, and methanol, although a relatively poor proton donor, is toward certain acceptors a better donor than the other alcohols studied (*22*, *23*). The results for methanol include some negative contributions due to the $\mathrm{O{=}S{=}O\cdots H{-}O}$ hydrogen bonding. In the mixtures of the higher alcohols these contributions appear to be extremely small, and the very large values of H^E_m suggest that the positive contributions due to the breakup of interactions between the molecules of DEMSA are overwhelming.

Finally, a comparison of the present results with those for the mixtures of the same alcohols with the considerably better proton acceptor, *N*,*N*-dimethylacetamide (DMA) is in order. As one would expect on the basis of the proton-accepting abilities of DEMSA and DMA the excess enthalpies are much greater for DEMSA than for DMA (*1*). While the values for all DEMSA–alcohol systems studied are positive and large in magnitude, those for the DMA–methanol system are noticeably negative (H^E_m(min) ≈ −750 J mol^{-1} at 313.15 K), those for the DMA–ethanol and DMA–2-methyl-2-propanol systems change sign, and those for the mixtures of DMA with 1-propanol, 2-propanol, and 1-butanol are moderately positive (H_m(max) ≈ 190, 460, and 320 J mol^{-1} at 313.15 K, respectively).

Registry No. $CH_3SO_2N(C_2H_5)_2$, 2374-61-0; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-methyl-2-propanol, 75-65-0.

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Excess Volumes of Binary Solvent Mixtures of *N*,*N*-Diethylmethanesulfonamide with Aliphatic Alcohols

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Molar excess volumes were determined, by density measurements, for binary solvent mixtures of *N*,*N*-diethylmethanesulfonamide (DEMSA) with methanol at 303.15 K and with ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 and 333.15 K. The excess volumes of the primary alcohols increase with the length of the alkyl chain and are smaller at 303.15 K than at 333.15 K. The values are negative for methanol, mainly negative for ethanol, and positive for 1-propanol, 2-propanol, and 1-butanol. 2-Methyl-2-propanol behaves exceptionally in having positive excess volumes at 303.15 K and mainly negative values at 333.15 K. The role of intermolecular interactions and geometrical effects is discussed through a comparison of the results with the excess enthalpies for the same mixtures.

Introduction

In earlier studies (*1*–*5*) we have determined the excess volumes for binary mixtures of aliphatic alcohols with *N*,*N*-dimethyl- and *N*-methyl-substituted acetamides and methanesulfonamides. Because of the high melting point (323 K) of *N*,*N*-dimethylmethanesulfonamide, the measurements for this amide were carried out at 333.15 K. For the same reason this amide was not suitable for our subsequent studies on excess enthalpies. The *N*,*N*-diethyl-substituted analogue, *N*,*N*-diethylmethanesulfonamide, $CH_3SO_2N(C_2H_5)_2$, which is liquid at room temperature, was accordingly chosen as the sulfonamide component for the excess enthalpy measurements (*6*). Here we report the molar excess volumes for binary solvent mixtures of DEMSA with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 and 333.15 K (for methanol only at 303.15 K). Our interest was to compare the

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