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 O=S=O···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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Table I. Densities ρ of the Pure Compounds

compound	ρ/(g cm^{-3}) 303.15 K	ρ/(g cm^{-3}) 333.15 K
methanol	0.781 82	
ethanol	0.780 74	0.754 38
1-propanol	0.795 61	0.770 64
2-propanol	0.776 59	0.749 33
1-butanol	0.801 91	0.778 22
2-methyl-2-propanol	0.775 46	0.743 18
DEMSA	1.092 26	1.065 32

Table II. Molar Excess Volumes V_m^E of Binary Mixtures of DEMSA with Aliphatic Alcohols[a]

	V_m^E/(cm^3 mol^{-1})			V_m^E/(cm^3 mol^{-1})	
x	303.15 K	333.15 K	x	303.15 K	333.15 K
			Methanol		
0.0650	-0.173		0.5148	-0.269	
0.1394	-0.267		0.5856	-0.222	
0.2155	-0.307		0.6922	-0.167	
0.2885	-0.321		0.7686	-0.130	
0.3717	-0.306		0.8304	-0.090	
0.4509	-0.287		0.9084	-0.062	
			Ethanol		
0.0656	-0.091	-0.057	0.5135	-0.111	-0.064
0.1402	-0.139	-0.099	0.5968	-0.083	-0.057
0.2228	-0.159	-0.120	0.6622	-0.071	-0.037
0.2849	-0.166	-0.124	0.7430	-0.033	-0.013
0.3659	-0.144	-0.099	0.8454	-0.023	0.003
0.4606	-0.124	-0.077	0.9395	-0.004	0.004
			1-Propanol		
0.0661	0.021	0.053	0.5219	0.094	0.166
0.1423	0.035	0.086	0.5944	0.097	0.164
0.2148	0.057	0.122	0.6850	0.094	0.154
0.3057	0.070	0.138	0.7587	0.073	0.120
0.3821	0.082	0.152	0.8085	0.063	0.109
0.4421	0.092	0.161	0.8907	0.040	0.075
			2-Propanol		
0.0680	0.033	0.050	0.5136	0.099	0.124
0.1441	0.062	0.085	0.5952	0.090	0.108
0.2157	0.077	0.112	0.6857	0.087	0.098
0.2582	0.089	0.122	0.7556	0.072	0.078
0.3391	0.101	0.136	0.8417	0.052	0.065
0.4088	0.100	0.130	0.9259	0.030	0.034
0.4524	0.101	0.123			
			1-Butanol		
0.0631	0.078	0.099	0.5227	0.227	0.289
0.1404	0.128	0.182	0.6053	0.201	0.253
0.2197	0.167	0.235	0.6908	0.185	0.232
0.2937	0.181	0.254	0.7579	0.172	0.207
0.3626	0.204	0.280	0.8437	0.125	0.162
0.4515	0.215	0.285	0.9281	0.071	0.083
			2-Methyl-2-propanol		
0.0764	0.088	-0.082	0.5369	0.262	-0.017
0.1463	0.130	-0.108	0.6062	0.265	0.006
0.2364	0.204	-0.107	0.6888	0.247	0.018
0.3171	0.227	-0.074	0.7621	0.235	0.017
0.3944	0.254	-0.046	0.8534	0.150	0.029
0.4712	0.253	-0.031	0.9381	0.062	0.018

[a] x is the mole fraction of DEMSA.

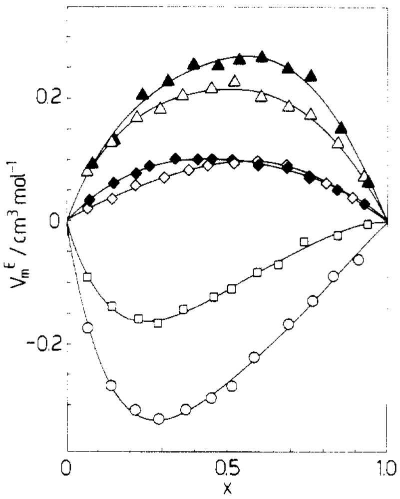

Figure 1. Excess volumes V_m^E of the mixtures of DEMSA with aliphatic alcohols at 303.15 K vs. the mole fraction x of DEMSA: (○) methanol; (□) ethanol; (◇) 1-propanol; (◆) 2-propanol; (△) 1-butanol; (▲) 2-methyl-2-propanol.

excess volumes with the excess enthalpies for the same mixtures, as this was expected to provide insight into the relative importance of the contributions due to intermolecular interactions and those due to geometrical effects.

Experimental Section

Materials. The alcohols were the same as in the previous studies (*6*, *7*). *N*,*N*-Diethylmethanesulfonamide was prepared and purified as described earlier (*6*).

Measurements. Densities were measured with a digital density meter DMA 40 (Anton Paar K.G., Austria) with a reproducibility of within ±0.0001 g cm^{-3}. The measured densities of the pure compounds are reported in Table I.

Results and Discussion

The molar excess volumes V_m^E were calculated from the densities of the pure components and the mixtures with the equation

$$V_m^E = \frac{(1-x)M_1 + xM_2}{\rho} - \frac{(1-x)M_1}{\rho_1} - \frac{xM_2}{\rho_2} \qquad (1)$$

where x is the mole fraction of DEMSA, ρ is the density of the mixture, ρ_1 and ρ_2 are the densities, and M_1 and M_2 are the molar masses of the alcohol and DEMSA, respectively.

The excess volumes are collected in Table II and are also represented graphically as functions of x in Figures 1 and 2. To each set of excess volumes we fitted the equation

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \qquad (2)$$

Table III. Coefficients A_i of Eq 2 and the Standard Deviations $\sigma(V_m^E)$

DEMSA +	T/K	A_0	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$/(cm^3 mol^{-1})
methanol	303.15	-1.0772	-0.8522	-0.2571	-0.4349	-0.9184	0.004
ethanol	303.15	-0.4557	-0.5865	-0.2637	-0.2593	-0.2225	0.005
	333.15	-0.2825	-0.5019	-0.4133	-0.1763	0.3364	0.005
1-propanol	303.15	0.3811	-0.1236	-0.0429	0.1179		0.003
	333.15	0.6638	-0.0614	0.00872	0.1438	0.2481	0.004
2-propanol	303.15	0.3996	0.0852	0.1034	-0.0459		0.002
	333.15	0.4921	0.2379	0.1985	-0.1425		0.003
1-butanol	303.15	0.8741	-0.0127	-0.00014	0.1619	0.5654	0.005
	333.15	1.1284	0.1966	0.2459	0.00638	0.3528	0.006
2-methyl-2-propanol	303.15	1.0395	-0.1972	0.7150	0.2628	-0.8524	0.006
	333.15	-0.0806	-0.5038	-0.4987	-0.5216		0.004

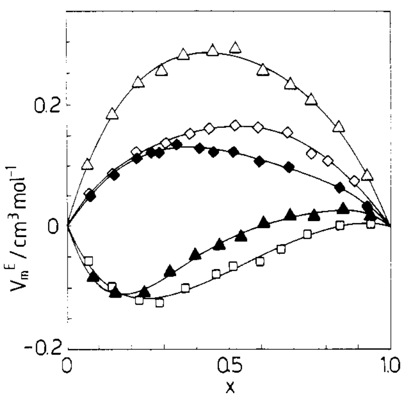

Figure 2. Excess volumes V_m^E of the mixtures of DEMSA with aliphatic alcohols at 333.15 K. The symbols are the same as in Figure 1.

Coefficients A_i of these fitting equations together with the standard deviations $\rho(V_m)$ of the fits are collected in Table III.

The excess volumes of the primary alcohols increase with the length of the alkyl chain and are smaller at the lower temperature than at the higher; the values range between −0.32 and 0.23 cm^3 mol^{-1} at 303.15 K and between −0.17 and 0.29 cm^3 mol^{-1} (methanol not measured) at 333.15 K. For 2-methyl-2-propanol, however, the values are positive at 303.15 K, but mainly negative at 333.15 K.

In the present mixtures, considerable amounts of positive contributions are expected due to the break-up of interactions between like molecules, viz., the rupture of the hydrogen-bonded chains of the alcohols and the loosening of the dipolar interactions between the amide molecules. The results indicate, however, that negative contributions predominate in the mixtures of methanol and ethanol with DEMSA. One source of negative contributions is the interactions between unlike molecules. However, since the alcohols are relatively poor proton donors (*8*, *9*) and the sulfonamides are relatively poor proton acceptors (*10*–*12*), we think that the contributions due to the DEMSA–alcohol heteroassociation equilibria are in no way sufficient to override the positive contributions. The more important source of the negative contributions may be the differences in the size and shape of the components of the mixtures. The molar volumes of DEMSA, methanol, and ethanol at 303.15 K are 138.45, 40.98, and 59.01 cm^3 mol^{-1}, respectively, which might allow the components to fit into each others' structures, so that reduction in volume occurs.

Comparison of the excess volumes with the excess enthalpies for the same mixtures supports this conclusion. The excess enthalpies, which are less sensitive to geometrical effects than are the excess volumes, are positive and great in magnitude, suggesting that as far as intermolecular interactions are concerned the break-up of interactions between like molecules predominates in all present amide–alcohol systems.

The molar volumes of the higher alcohols are greater (75.53, 92.42, 77.39, and 95.58 cm^3 mol^{-1} at 303.15 K for 1-propanol, 1-butanol, 2-propanol, and 2-methyl-2-propanol, respectively) and their proton-accepting abilities are smaller than those of methanol. As a result, the negative contributions to the excess volumes are relatively smaller for the mixtures of the higher alcohols than for the mixtures of methanol and are not sufficient to override the positive contributions. However, the magnitudes of the excess volumes are relatively small compared with the excess enthalpies and suggest that also in the mixtures of the higher alcohols there are negative contributions of geometrical origin. The fact that the excess volumes for the DEMSA–2-methyl-2-propanol system are positive at 303.15 K but mainly negative at 333.15 K seems, further, to be related to structural effects due to the globular shape of the 2-methyl-2-propanol molecule.

Registry No. DEMSA, 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 Ethanol + Water at 298.15 and 323.15 K at Pressures up to 220 MPa

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Excess volumes of ethanol + water mixtures at 298.15 and 323.15 K have been determined by a direct method in a mixing dilatometer at pressures up to 220 MPa. These measurements are reported and compared with relevant published data.

Introduction

The volumetric behavior of ethanol + water in the liquid phase at normal pressure has been the subject of extensive study over the years. The reader is referred to papers by Westmeier (*1*), Marsh and Richards (*2*), and Benson and Kiyohara (*3*) for relatively recent measurements and reviews.

The only significant measurements at high pressure appear to be those of Hamann and Smith (*4*), Moriyoshi et al. (*5*, *6*),

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