determined primarily by the number of water molecules in the first solvation shell, and not by specific solute–solvent interactions.

Glossary

ΔH°	the standard enthalpy of solution; it is assumed that the solutions are sufficiently dilute that the standard state of an ideal 1 m solution, pressure of 1 atm, applies
ΔC_p°	the standard heat capacity change upon solution (the first derivative of the standard enthalpy of solution with respect to temperature)
θ	an arbitrary reference temperature used in the Taylor's series calculation of the temperature dependence of the enthalpy of solution
N	the number of water molecules in the first solvation shell
R	the gas constant
ΔH_{sh}	in eq 2, the energy difference between the two states in which water molecules in the first solvation shell can exist
τ	the reciprocal temperature $(1/T)$, K^{-1}
τ_m	the reciprocal temperature at which the populations of the two states are equal

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Excess Molar Enthalpies of Seven *n*-Hexadecane + *n*-Alkylamine Binary Liquid Mixtures

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An isobaric and quasi-isothermic calorimeter has been used to determine excess molar enthalpies, H^E, as a function of concentration at atmospheric pressure and 303.15 K for seven binary liquid mixtures containing *n*-alkylamine (*n*-propyl-, *n*-butyl-, *n*-hexyl-, *n*-octyl-, *n*-decyl-, *n*-dodecyl-, and *n*-pentadecylamine) with *n*-hexadecane. The maxima of the H^E–composition curves decrease with increasing length of the aliphatic chain of amine and shift gradually toward the hexadecane-rich side.

Table I. Refractive Indices of Pure Amines

compound	$n^{298.15}{}_D$ this work	lit. (8)
n-propylamine	1.385 05	1.3851
n-butylamine	1.398 75	1.3987
n-hexylamine	1.416 11	1.4167
n-octylamine	1.427 03	1.4277
n-decylamine	1.434 80	1.4352
n-dodecylamine	1.433 98[a]	1.4406
n-pentadecylamine	1.439 54[a]	1.4464

[a] At 313.15 K.

Introduction

Measurements of thermodynamic properties on *n*-alkane + *n*-alkylamine have been reported extensively (*1–3*), but no suitable data are available in the literature for amines whose aliphatic radical has more than eight carbon atoms. We report here the excess molar enthalpy, H^E, at 303.15 K, for *n*-hexadecane ($C_{16}H_{34}$) + *n*-propylamine (PrNH₂), + *n*-butylamine (BuNH₂), + *n*-hexylamine (HeNH₂), + *n*-octylamine (OcNH₂), + *n*-decylamine (DeNH₂), and + *n*-dodecylamine (DoNH₂), and for $C_{16}H_{34}$ + *n*-pentadecylamine (PeNH₂) at 313.15 K. As far as we know, the only previous measurements on these mixtures are those of Pfestorf et al. (*1*) of H^E for $C_{16}H_{34}$ + BuNH₂, + HeNH₂, and + OcNH₂; their results (1838, 1508, and 1292 J mol⁻¹, respectively, at 298.15 and $x = 0.5$) are higher than ours (1731, 1433, and 1146 J mol⁻¹, respectively, at 303.15 K). Although we cannot be sure of the cause of these discrepancies, we point out that impurities in amines can be an important source of error.

Experimental Section

All the liquids used were from Fluka AG, Buchs, better than 99 mol %, except PeNH₂ which is better than 98 mol %. *n*-Propylamine, *n*-butylamine, and *n*-hexylamine were purified by a low-pressure distillation method described elsewhere (*4*). No further purification was made with the other liquids, although they were kept over activated molecular sieve to avoid moisture contamination. Refractive indices (Table I) and static dielectric constants of the pure liquids (*3*) agree satisfactorily with those in literature.

Excess molar enthalpies were determined by using an isobaric and quasi-isothermic calorimeter similar to that described in ref *5*. The mixing cell is an anchor-shaped glass receptacle filled under vacuum with bidistillated Hg to isolate weighed quantities of the two liquids in the limbs of the cell. A continuous pendular movement permits the two liquids to mix at constant pressure and in the complete absence of vapor phase. Electrical energy was measured to better than 0.5%, and

Table II. Excess Molar Enthalpies (H^E) for n-Hexadecane + n-Alkylamine at 303.15 K

x	H^E, J mol^{-1}	x	H^E, J mol^{-1}	x	H^E, J mol^{-1}
		$(x)n$-C$_3$H$_7$NH$_2$ + $(1-x)n$-C$_{16}$H$_{34}$			
0.0660	404	0.4441	1812	0.8107	1310
0.0979	575	0.5233	1887	0.8739	980
0.1981	1069	0.5413	1888	0.9452	475
0.3024	1476	0.5984	1877		
0.3962	1732	0.6997	1718		
		$(x)n$-C$_4$H$_9$NH$_2$ + $(1-x)n$-C$_{16}$H$_{34}$			
0.0660	379	0.3963	1629	0.6958	1544
0.1341	750	0.4464	1704	0.7831	1305
0.1978	1028	0.5053	1739	0.8603	971
0.3043	1398	0.5484	1733	0.9128	670
0.3460	1515	0.6050	1687	0.9611	334
		$(x)n$-C$_6$H$_{13}$NH$_2$ + $(1-x)n$-C$_{16}$H$_{34}$			
0.0478	234	0.3977	1351	0.6949	1256
0.1301	607	0.4493	1410	0.7943	998
0.1977	870	0.4925	1417	0.8029	969
0.3052	1191	0.5474	1433	0.8624	737
0.3420	1274	0.6331	1354	0.9280	432
		$(x)n$-C$_8$H$_{17}$NH$_2$ + $(1-x)n$-C$_{16}$H$_{34}$			
0.0629	248	0.3898	1089	0.6033	1095
0.1309	484	0.4186	1113	0.6906	985
0.1994	709	0.4632	1139	0.7778	804
0.2948	949	0.5109	1144	0.8184	686
0.3414	1029	0.5374	1134	0.8992	412
		$(x)n$-C$_{10}$H$_{21}$NH$_2$ + $(1-x)n$-C$_{16}$H$_{34}$			
0.0649	221	0.3975	937	0.6334	879
0.1331	445	0.4563	964	0.7063	787
0.1997	617	0.4954	970	0.7972	614
0.2984	818	0.5548	938	0.8553	478
0.3323	870	0.5985	908	0.9248	266
		$(x)n$-C$_{12}$H$_{25}$NH$_2$ + $(1-x)n$-C$_{16}$H$_{34}$			
0.0673	207	0.3981	820	0.6854	702
0.1328	402	0.4509	849	0.7986	522
0.2019	562	0.4798	841	0.8635	376
0.2958	722	0.5432	825	0.9403	170
0.3459	786	0.5964	794		
		$(x)n$-C$_{15}$H$_{31}$HN$_2$ + $(1-x)n$-C$_{16}$H$_{34}$^{a}			
0.0318	68	0.4544	619	0.7984	361
0.0778	170	0.4877	620	0.8887	220
0.1433	306	0.5436	605	0.9435	115
0.2537	486	0.5461	606		
0.3431	590	0.6848	500		

^{a}At 313.15 K.

temperature in the water bath was controlled to within ±0.002 K. The estimated errors are $\delta x < 0.0002$; δT (reproducibility) = 0.01 K (*6*). The calorimeter was checked against hexane + cyclohexane, at 298.15 K, the agreement with the data reported (*7*) being better than 0.5% over the central range of concentrations.

Results and Discussion

The values of H^E for C$_{16}$H$_{34}$ + PrNH$_2$, + BuNH$_2$, + HeNH$_2$, + OcNH$_2$, + DeNH$_2$, and + DoNH$_2$ at 303.15 K, and for C$_{16}$H$_{34}$ + PeNH$_2$ at 313.15 K, over the whole mole fraction range are given in Table II. The composition dependence of H^E was correlated by the polynomial

$$H^E/(\text{J mol}^{-1}) = x(1-x) \sum_{i=0}^{n} a_i(1-2x)^i \tag{1}$$

where x is the mole fraction of n-alkylamine. The a_i parameters were obtained by least squares and are collected in Table III, together with the standard deviations $\sigma(H^E)$ calculated as

$$\sigma(H^E) = [\sum(\delta H^E)^2/(N-\alpha)]^{1/2}$$

where δH^E are the deviations of the experimental values from

Table III. Parameters a_i of Eq 1 for n-Hexadecane + n-Alkylamine and Standard Deviations $\sigma(H^E)$ at 303.15 K

mixture	a_0	a_1	a_2	a_3	$\sigma(H^E)$
$(1-x)n$-C$_{16}$H$_{34}$ +					
$(x)n$-C$_3$H$_7$NH$_2$	7500	-1471	418	-50	5
$(x)n$-C$_4$H$_9$NH$_2$	6902	-654	665	-1026	9
$(x)n$-C$_6$H$_{13}$NH$_2$	5732	-308	151	-570	6
$(x)n$-C$_8$H$_{17}$NH$_2$	4601	-62	-272	-222	7
$(x)n$-C$_{10}$H$_{21}$NH$_2$	3862	251	-104	-488	5
$(x)n$-C$_{12}$H$_{25}$NH$_2$	3391	301	-211	-194	7
$(x)n$-C$_{15}$H$_{31}$NH$_2$^{a}	2490	437	-307	-479	4

^{a}At 313.15 K.
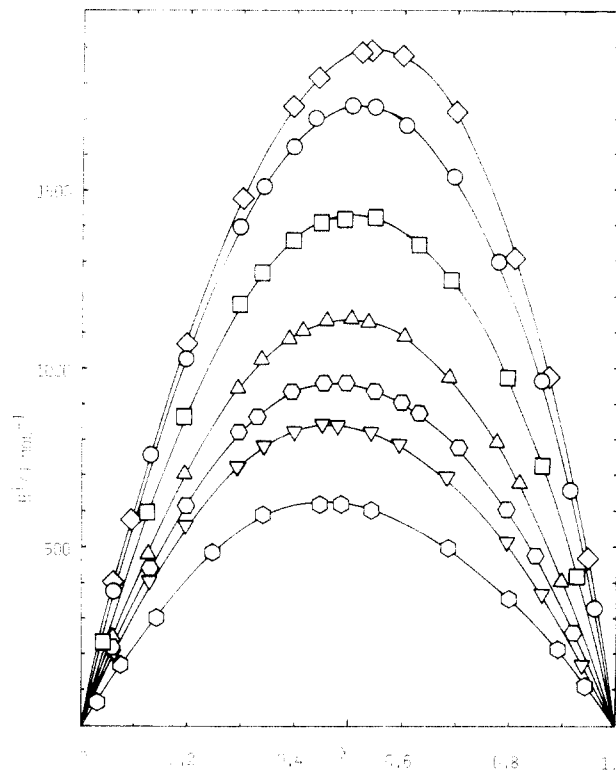
Figure 1. Excess molar enthalpies H^E(303.15 K) of n-C$_{16}$H$_{34}$ + ($\Diamond$) n-C$_3$H$_7$NH$_2$; (O) n-C$_4$H$_9$NH$_2$; ($\square$) n-C$_6$H$_{13}$NH$_2$; ($\triangle$) n-C$_8$H$_{17}$NH$_2$; (O) n-C$_{10}$H$_{21}$NH$_2$; ($\triangledown$) n-C$_{12}$H$_{25}$NH$_2$; (O) n-C$_{15}$H$_{31}$NH$_2$ (313.15 K).

the fitted ones, N is the total number of measurements, and α is the number of coefficients of the fitted equations. The H^E values are plotted against x in Figure 1. It is clear both from Table II and from Figure 1 that the H^Es are all positive and decrease with increasing length of the aliphatic chain of n-alkylamine; at the same time, the maxima of the curves H^E-x shift gradually toward the hexadecane-rich side.

Glossary

a_i	coefficients in representation of H^E by eq 1
H^E	excess molar enthalpy, J mol^{-1}
n_D	refractive index
x	mole fraction of n-alkylamine
α	number of coefficients in eq 1
$\sigma(H^E)$	standard deviation of least-squares representation by eq 1, J mol^{-1}

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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

$$H_m^E/(J\ mol^{-1}) = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \qquad (1)$$

Coefficients A_i of these fitting equations together with the standard deviations $\sigma(H_m^E)$ 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_1^E) and the amide (H_2^E) from the equations

$$H_1^E = H_m^E - x\left(\frac{\partial H_m^E}{\partial x}\right)_{p,T} \qquad (2)$$

$$H_2^E = H_m^E + (1-x)\left(\frac{\partial H_m^E}{\partial x}\right)_{p,T} \qquad (3)$$

The curves of H_1^E and H_2^E as functions of x are plotted in Figure 2.

The values of H_m^E, H_1^E, and H_2^E are positive over the whole composition range for all the DEMSA–alcohol mixtures studied. In all $H_m^E(x)$ curves the maximum is large in magnitude and lies at about $x = 0.5$. For the primary alcohols it increases with