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Excess Enthalpies of 1-Heptanol + *n*-Alkane and Di-*n*-propylamine + Normal Alcohol Mixtures at 298.15 K

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The excess molar enthalpies of the binary liquid mixtures 1-heptanol + *n*-alkane (C_6–C_{10}) and di-*n*-propylamine + normal alcohol (C_4–C_8) have been determined at atmospheric pressure and 298.15 K as a function of mole fraction. The apparatus used was a standard Calvet microcalorimeter equipped with a device allowing the exclusion of a vapor phase. The mixtures 1-heptanol + *n*-alkane are endothermic ($H^E > 0$), and the values of the excess molar enthalpies increase with length of the hydrocarbon chain of the alkane. For di-*n*-propylamine + normal alcohol mixtures the excess enthalpy H^E is negative (highly exothermic) and its absolute value diminishes very slightly with the increase of length of the hydrocarbon chain of the alcohol.

Introduction

Although the thermodynamic properties of binary liquid mixtures of alcohols with alkanes have lately been the subject of a considerable amount of research (*1*–*5*), only the initial members of the alkane series have been investigated with 1-heptanol. In order to make available more systematic data concerning these systems, we have determined the excess molar enthalpies of mixtures of 1-heptanol with higher order alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane).

The second part of the work presented here is one of the few studies so far made of liquid mixtures of alcohols with amines. The complexity of these systems has hitherto discouraged their systematic investigation. As a step toward understanding such aspects as the possible associations between amine and alcohol groups, we have determined the excess molar enthalpies of the binary mixtures di-*n*-propylamine (+ 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol).

Experimental Section

The chemical products used were supplied by Fluka (Buchs, Switzerland). All were better than 99 mol % pure as supplied except the 1-pentanol, which was purified before use by triple distillation in a rectifying column, the final purity being 99.5 mol %. The densities of all the chemicals were measured with an Anton Paar Model DMA 602 oscillatory densimeter and their refractive indices at 298.15 K with a Zeiss Model 67097 refractometer. In both cases the temperature was kept constant to within ±5 × 10^{-3} K. All chemicals were kept under molecular sieves (Union Carbide Type 4Å, 2.5–1.4 mm; beads from Fluka) and were partially degasified before use. The purity of the substances is shown by the measured values agreeing with published densities (*6*, *7*), and refractive indices (*6*, *8*), to within ±0.04% and ±0.014%, respectively (Tables I and II).

Excess molar enthalpies were determined by using a Calvet calorimeter (*9*) with a 10-cm^3 stainless steel cell and a device (*10*) allowing the exclusion of a vapor phase during use. The temperature of the calorimeter was thermostated to within ±5 × 10^{-3} K and its response to mixing, proportional to the heat developed in the cell, was obtained with a Hewlett-Packard 3373 B integrator. The calorimeter was calibrated electrically by Joule effect, and chemically by determining the excess molar enthalpy at 298.15 K of the hexane + cyclohexane mixture proposed by Stokes et al. (*11*) as a calorimetric standard and adopted by the IUPAC (*12*). The discrepancy between our results and those of Stokes et al. (*11*) was less than 1%.

Table I. Densities (ρ) of Pure Components at 298.15 K

	$\rho/(kg\ m^{-3})$	
liquid	this work	lit. at 298.15 K
n-hexane	654.72	654.81 (*6*)
n-heptane	679.58	679.51 (*6*)
n-octane	698.73	698.49 (*6*)
n-nonane	714.03	713.81 (*6*)
n-decane	726.51	726.25 (*6*)
1-butanol	806.07	806.0 (*6*)
1-pentanol	811.50	811.5 (*6*)
1-hexanol	815.68	815.9 (*6*)
1-heptanol	818.96	818.6 (*7*)
1-octanol	822.07	822.09 (*6*)
di-*n*-propylamine	733.21	732.9 (*6*)

Table II. Refractive Indices (n_D) of Pure Components at 298.15 K

	n_D	
liquid	this work	lit. at 298.15 K
n-hexane	1.372 15	1.372 26 (*6*)
n-heptane	1.385 03	1.385 11 (*6*)
n-octane	1.384 98	1.395 05 (*6*)
n-nonane	1.403 08	1.403 11 (*6*)
n-decane	1.409 56	1.409 67 (*6*)
1-butanol	1.397 22	1.397 26 (*6*)
1-pentanol	1.407 94	1.407 96 (*6*)
1-hexanol	1.415 84	1.415 80 (*6*)
1-heptanol	1.422 57	1.424 9 (*8*)[a]
1-octanol	1.427 45	1.427 50 (*6*)
di-*n*-propylamine	1.402 0	1.401 8 (*6*)

[a] Value at 293.15 K.

Results and Discussion

The results of our measurements of H^E for the five 1-heptanol + *n*-alkane mixtures studied are shown in Table III, and those of the di-*n*-propylamine + normal alcohol mixtures in Table IV. In Table III x represents the mole fraction of 1-heptanol, and in Table IV the mole fraction of di-*n*-propylamine. A variable-degree empirical equation of the form

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

has been fitted to the results, where, following Jones et al. (*13*), $z = x^{1/2}$ for the 1-heptanol + *n*-alkane systems, whose curves are asymmetrical, and $z = 2x - 1$ for the di-*n*-propylamine + normal alcohol systems, as suggested by Redlich and Kister (*14*) (x being the mole fraction of the unchanging component in each series). The number of parameters A_i employed in

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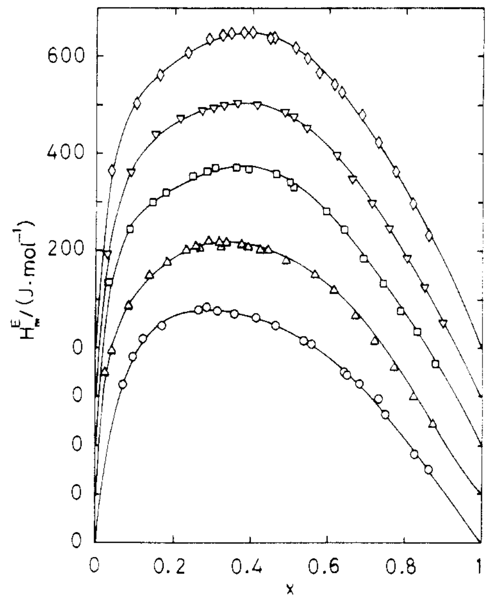

Figure 1. Excess enthalpy H^E plotted against mole fraction of *n*-alkane at 298.15 K for the mixtures 1-heptanol with *n*-alkane: (O) hexane, (△) heptane, (□) octane, (▽) nonane, (◇) decane.

Table III. Molar Excess Enthalpy H^E for 1-Heptanol + *n*-Alkane at 298.15 K

x	H^E/ (J·mol^{-1})	x	H^E/ (J·mol^{-1})	x	H^E/ (J·mol^{-1})
$xC_7H_{15}OH + (1 - x)C_6H_{14}$					
0.0698	323	0.3578	469	0.6511	343
0.0957	381	0.4143	461	0.6829	325
0.1220	418	0.4646	444	0.7326	294
0.1702	445	0.5382	413	0.7509	259
0.2652	477	0.5574	406	0.8255	180
0.2863	483	0.6421	350	0.8632	149
0.3135	475				
$xC_7H_{15}OH + (1 - x)C_7H_{16}$					
0.0242	249	0.2912	518	0.4910	478
0.0413	294	0.3180	516	0.5665	449
0.0837	386	0.3223	508	0.6158	417
0.1377	448	0.3367	517	0.6709	366
0.1841	475	0.3766	511	0.7220	313
0.2327	500	0.3942	507	0.7727	258
0.2582	508	0.4240	504	0.8229	199
0.2686	502	0.4450	500	0.8736	142
$xC_7H_{15}OH + (1 - x)C_8H_{18}$					
0.0376	334	0.3644	570	0.6470	444
0.0915	444	0.3978	566	0.6963	383
0.1493	500	0.4698	557	0.7483	332
0.1821	519	0.5049	539	0.7934	275
0.2526	553	0.5153	531	0.8358	233
0.2893	564	0.6002	481	0.8843	165
0.3109	572				
$xC_7H_{15}OH + (1 - x)C_9H_{20}$					
0.0326	292	0.3673	602	0.6653	446
0.0926	461	0.4182	599	0.7155	397
0.1563	539	0.4900	584	0.7617	344
0.2191	571	0.5128	575	0.8074	283
0.2754	587	0.5462	551	0.8537	223
0.3058	592	0.6251	495	0.9017	151
0.3324	598				
$xC_7H_{15}OH + (1 - x)C_{10}H_{22}$					
0.0409	364	0.3827	649	0.6176	542
0.1051	503	0.4058	650	0.6367	525
0.1660	562	0.4508	636	0.6888	480
0.2385	607	0.4603	638	0.7324	423
0.2935	635	0.5164	617	0.7775	363
0.3292	643	0.5470	595	0.8224	296
0.3512	648	0.5782	565	0.8639	231

Table IV. Molar Excess Enthalpy H^E for Di-*n*-propylamine + Normal Alcohol at 298.15 K

x	H^E/ (J·mol^{-1})	x	H^E/ (J·mol^{-1})	x	H^E/ (J·mol^{-1})
$x(C_3H_7)_2NH + (1 - x)C_4H_9OH$					
0.0497	−554	0.3115	−2317	0.5474	−2349
0.0873	−914	0.3366	−2378	0.5763	−2276
0.1263	−1249	0.3659	−2407	0.6177	−2142
0.1664	−1556	0.3775	−2457	0.6506	−2008
0.2087	−1847	0.4230	−2480	0.6993	−1810
0.2322	−1986	0.4499	−2469	0.7542	−1532
0.2579	−2122	0.4874	−2424	0.8161	−1201
0.2871	−2245	0.5151	−2410	0.8902	−752
$x(C_3H_7)_2NH + (1 - x)C_5H_{11}OH$					
0.0638	−622	0.3276	−2382	0.5587	−2322
0.1037	−1044	0.3688	−2445	0.5925	−2238
0.1467	−1382	0.3770	−2485	0.6243	−2109
0.1912	−1739	0.4075	−2460	0.6674	−1944
0.2374	−1990	0.4275	−2498	0.7284	−1673
0.2662	−2146	0.4615	−2494	0.7834	−1386
0.2923	−2251	0.4948	−2450	0.8421	−1055
0.3203	−2341	0.5246	−2412	0.8964	−713
$x(C_3H_7)_2NH + (1 - x)C_6H_{13}OH$					
0.0726	−717	0.3814	−2346	0.5891	−2156
0.1198	−1133	0.4113	−2377	0.6453	−1994
0.1642	−1485	0.4381	−2370	0.7009	−1776
0.2130	−1785	0.4448	−2374	0.7494	−1557
0.2633	−2037	0.4927	−2378	0.8062	−1233
0.3098	−2174	0.5012	−2363	0.8626	−914
0.3199	−2227	0.5306	−2253	0.9124	−613
0.3499	−2296	0.5550	−2280		
$x(C_3H_7)_2NH + (1 - x)C_7H_{15}OH$					
0.0844	−772	0.4141	−2315	0.6959	−1759
0.1316	−1172	0.4411	−2336	0.7244	−1634
0.1844	−1536	0.4745	−2333	0.7723	−1398
0.2366	−1861	0.5312	−2261	0.8237	−1115
0.2856	−2030	0.5648	−2169	0.8746	−828
0.3201	−2144	0.5919	−2104	0.9252	−516
0.3570	−2237	0.6212	−2051		
0.3821	−2308	0.6676	−1865		
$x(C_3H_7)_2NH + (1 - x)C_8H_{17}OH$					
0.0859	−770	0.3759	−2137	0.6315	−1961
0.1471	−1242	0.4101	−2207	0.6785	−1783
0.2006	−1561	0.4172	−2220	0.7077	−1651
0.2226	−1681	0.4420	−2231	0.7474	−1493
0.2611	−1804	0.4708	−2205	0.7914	−1287
0.3102	−2005	0.5036	−2191	0.8383	−1041
0.3414	−2124	0.5852	−2102	0.8806	−752
0.3446	−2115	0.6156	−2018		

each case was determined by using an *F* test to estimate the significance of the additional term (*15*). The values of A_i calculated and the corresponding standard deviations $\sigma(H^E)$ for each mixture are shown in Table V. Figures 1 and 2 show the enthalpy–composition curves of, respectively, the 1-heptanol + *n*-alkane and di-*n*-propylamine + normal alcohol mixtures.

The three main characteristics of the alcohol + alkane series are the positive excess enthalpies, which show bond breaking to be the predominant phenomenon, the increase in H^E with the length of the alkane chain, and the asymmetry of the enthalpy–composition curves, whose maxima occur where the concentration of alcohol is less than that of alkane. Similar results have been reported by Nguyen et al. (*16*) for binary mixtures of butanol and octanol with the alkanes from hexane to decane, and by Brown et al. (*17*) for mixtures of octanol with hexane, heptane, and nonane. The asymmetry of the enthalpy–composition curves may be interpreted as reflecting the fact that whereas the addition of a small quantity of alcohol to an "inert" liquid may break all the hydrogen bonds present in the alcohol, a proportion of hydrogen bonds may remain unbroken when the mixture is rich in alcohol. According to published data (*18*, *19*), for a given alkane at a fixed temperature the excess enthalpy

Table V. Coefficients A_i and Standard Deviations $\sigma(H^E)$ for Representation of Excess Enthalpies H^E at 298.15 K by Eq 1

	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(H^E)$/ (J·mol^{-1})
$xC_7H_{15}OH$							
$+ (1 - x)C_6H_{14}$	11 316	−32 974	39 008	−16 335			6
$+ (1 - x)C_7H_{16}$	25 277	−151 066	429 850	−645 880	496 460	−153 949	6
$+ (1 - x)C_8H_{18}$	22 896	−106 261	213 827	−196 101	67 348		6
$+ (1 - x)C_9H_{20}$	19 874	−82 525	151 461	−126 950	39 752		4
$+ (1 - x)C_{10}H_{22}$	23 237	−104 373	205 972	−185 741	62 976		6
$x(C_3H_7)_2NH$							
$+ (1 - x)C_4H_9OH$	−9 730	2 899	234	−763			12
$+ (1 - x)C_5H_{11}OH$	−9 752	3 108	−297	−1 667	1 661		15
$+ (1 - x)C_6H_{13}OH$	−9 383	2 490	−107	−864	543		18
$+ (1 - x)C_7H_{15}OH$	−9 192	2 348	252	−1 108	563		14
$+ (1 - x)C_8H_{17}OH$	−8 852	1 652	477				18

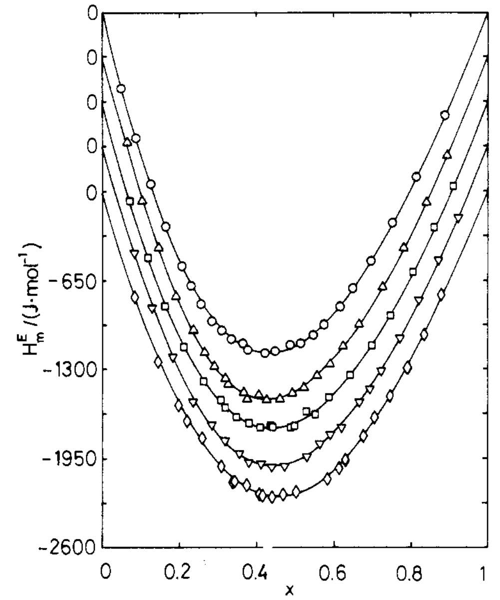

Figure 2. Excess enthalpy H^E plotted against mole fraction of normal alcohol at 298.15 K for the mixtures di-*n*-propylamine with normal alcohol: (○) 1-butanol, (△) 1-pentanol, (□) 1-hexanol, (▽) 1-heptanol, (◇) 1-octanol.

falls with the number of alcohol carbons, showing that the shorter the alcohol chain, the stronger are the interactions between the alcohol molecules. Our results fit in with this pattern. For example, the excess enthalpy H^E of the 1-heptanol + *n*-hexane mixture is intermediate between published values for 1-hexanol + *n*-hexane and 1-octanol + *n*-hexane. According to published data, H^E rises with temperature for a given mixture.

The secondary amine + alcohol mixtures have large negative excess enthalpies, reflecting the exothermic predominance of the formation of O–H···N and N–H···O bonds over the rupture of the O–H···O and N–H···N interactions present in the pure amine and alcohols. Similar results have been reported by others (*20–22*). The second noteworthy feature is that H^E is hardly affected by increasing the length of the alcohol chain, which shows that the variation in energy due to addition of a CH_2 unit is negligible compared with the factors mentioned above. Lastly, the maxima of the enthalpy–composition curves occur where the composition of amine is slightly less than that of alcohol. This may be interpreted as due to two factors, the symmetric rupture of alcohol–alcohol interactions, and the formation of 1:1 alcohol–amine complexes like those we have previously observed in analogous mixtures (*23*).

Registry No. $C_7H_{15}OH$, 111-70-6; $(C_3H_7)_2NH$, 142-84-7; C_6H_{14}, 110-54-3; C_7H_{16}, 142-82-5; C_8H_{18}, 111-65-9; C_9H_{20}, 111-84-2; $C_{10}H_{22}$, 124-18-5; C_4H_9OH, 71-36-3; $C_5H_{11}OH$, 71-41-0; $C_6H_{13}OH$, 111-27-3; $C_8H_{17}OH$, 111-87-5.

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