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Calorimetric Investigation of the Interactions of Some Hydrogen-Bonded Systems at 298.15 K

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The purpose of this work is to compare the enthalpies of hydrogen-bonded interactions involving a variety of proton donors and acceptors. Excess molar enthalpies H_m^E, as a function of mole fraction, are presented for single hydrogen-bonded systems involving propan-1-ol + dipropyl ether, + tripropylamine, + dipropyl sulfide, and + heptan-4-one, dipropylamine + dipropyl ether, + tripropylamine, + dipropyl sulfide, and + heptan-4-one, and propane-1-thiol + dipropyl ether, + tripropylamine, + dipropyl sulfide, and + heptan-4-one. Partial molar enthalpies at infinite dilution $H_{i,m}^E(x_i=0)$, calculated from an analysis of the data near $x_i = 0$, were used in an attempt to determine the relative strengths and propensities of the hydrogen-bonded interactions OH⋯O, OH⋯N, OH⋯S, NH⋯O, NH⋯N, NH⋯S, SH⋯O, SH⋯N, and SH⋯S. The component molecules are all fully propylated, thus localizing the source of the hydrogen-bonded interaction. For the systems involving a strong hydrogen donor, i.e., alkanol, the liquid phase hydrogen bond strength order mirrors that calculated for interactions in the gas phase from *ab initio* molecular orbital theory. In the systems involving a relatively weak hydrogen donor, i.e., secondary amine and a thiol, the hydrogen bond strength appears to be related to the available surface area of the hydrogen acceptor atom.

Introduction

Bricknell *et al.* (1995) have recently calculated the energies of interaction between gas phase hydrogen-bonded systems involving methanol, dimethylamine or methanethiol with one of dimethyl ether, trimethylamine or dimethyl sulfide, using *ab initio* molecular orbital theory and the GAUSSIAN-92 computer program (1992). In this work we compare enthalpies of hydrogen-bonded interactions involving a variety of proton donors and acceptors. We also compare the relative strengths and propensities of the hydrogen bonded interactions from the above-mentioned theoretical work for mixtures in the *gas phase* with similar properties for related species in the *liquid phase* obtained from excess enthalpy measurements presented here.

Van Ness *et al.* (1967) showed that, in alcohol + hydrocarbon systems, the partial molar enthalpies of mixing of alcohols at infinite dilution, $H_{i,m}^E(x_i=0)$ is approximately equal to the energies of hydrogen bonds in the alcohols. Similarly, Stokes *et al.* (1975) concluded that the limiting enthalpy of dilution of ethanol in alkanes and cycloalkanes represents essentially the enthalpy required to break all the hydrogen bonds present in the pure alcohol. Their findings are completed and presented elsewhere (Stokes *et al.*, 1980). We have extended the above approximations to describe bond strengths in mixtures containing two associated components, where one of the components shows a relatively weak self-association.

In this work, the analysis was performed on mixtures involving the OH⋯O, OH⋯N, OH⋯S, NH⋯O NH⋯N, NH⋯S, SH⋯O, SH⋯N, and SH⋯S hydrogen bonds. The liquids were chosen so that, for any pair of interacting species, only one hydrogen bond was possible. Furthermore, in an attempt to reduce the effect of different alkyl side chains, all monomer species are fully propylated.

In the work H_m^E values have been determined over the whole concentration range for mixtures of propan-1-ol + dipropyl ether (OH⋯O), + tripropylamine (OH⋯N), + dipropyl sulfide (OH⋯S), and + heptan-4-one (OH⋯O), for dipropylamine + dipropyl ether (NH⋯O), + tripropylamine (NH⋯N), + dipropyl sulfide (NH⋯S), and + heptan-4-one (NH⋯O), and for propane-1-thiol + dipropyl ether (SH⋯O), + tripropylamine (SH⋯N), + dipropyl sulfide (SH⋯S), and + heptan-4-one (SH⋯O). H_m^E values have also been determined for the following mixtures: heptane + propan-1-ol, + dipropyl ether, + dipropylamine, + tripropylamine, and + propane-1-thiol. Excess partial molar enthalpies at infinite dilution ($H_{i,m}^E(x_i=0)$, where i is the proton donor, have been calculated from experimental excess enthalpies, H_m^E, obtained from either reliable literature values or measurements described here.

Experimental Section

Propan-1-ol, dipropyl ether, dipropylamine, tripropylamine, dipropyl sulfide, heptan-4-one, and propane-1-thiol were obtained from Janssen Chimica. GC−MS revealed that the purity was greater than 98.7 mass % in all liquids except propane-1-thiol (96 mass %). Propan-1-ol was dried with magnesium metal activated with iodine, using the method of Lund and Bjerrum as described by Letcher *et al.* (1990). Both amines were distilled and dried with molecular sieves (type 4A, ±3.2 mm beads from Saarchem). Dipropyl ether (99.7 mass %), dipropyl sulfide, and propane-1-thiol were used without further purification due to the high cost of these liquids. Solvents were degassed prior to actual measurements. The mole fraction of water in each of the liquids was determined by Karl Fischer titration to be less than 0.001.

The excess molar enthalpies, H_m^E, were determined using a Thermometric 2277 thermal activity calorimeter. Results less than 0.05 mole fraction were obtained using a dilution procedure. The calorimeter was thermostated to ±0.005 K, and the measurements were made at 298.15 K.

Results

The H_m^E results of the determinations are shown in Tables 1−3. No literature values were found for the

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Table 1. Excess Molar Enthalpies H_m^E for x {$CH_3(CH_2)_2OH$, $(CH_3CH_2CH_2)_2NH$, or $CH_3CH_2CH_2SH$} + (1 − x) {$(CH_3CH_2CH_2)_2O$, $(CH_3CH_2CH_2)_3N$, or $(CH_3CH_2CH_2)_2S$} and the Deviations Δ Calculated from Eq 1 and the Parameters of Table 4

x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$	x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$	x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$
x Propan-1-ol + (1 − x) Dipropyl Ether								
0.00411	24.8	−1.2	0.205	697.7	−1.1	0.398	786.1	4.7
0.0153	91.1	−1.4	0.247	742.2	−1.4	0.514	731.5	0.1
0.0217	126.1	−4.0	0.268	755.0	−4.0	0.549	711.5	−5.2
0.0793	406.9	9.8	0.293	768.9	−3.2	0.580	672.1	−7.6
0.117	530.5	9.3	0.320	781.3	−0.4	0.797	378.4	−5.3
0.151	594.2	−11.7	0.376	789.7	5.1	0.856	279.0	−6.1
x Propan-1-ol + (1 − x) Tripropylamine								
0.0153	12.1	6.0	0.270	−111.1	3.1	0.730	−411.5	−8.2
0.0390	24.8	14.5	0.331	−156.3	4.9	0.800	−397.8	1.6
0.0981	−3.7	−2.8	0.460	−256.2	−0.8	0.870	−340.4	5.7
0.165	−42.1	−5.1	0.561	−322.1	1.0	0.912	−150.2	−3.8
0.210	−75.0	−6.4	0.656	−375.1	2.2			
x Propan-1-ol + (1 − x) Dipropyl Sulfide								
0.0904	587.3	15.5	0.400	1207.5	4.7	0.769	757.5	14.1
0.150	808.1	−6.8	0.457	1209.2	6.0	0.810	628.5	3.3
0.177	890.0	−9.1	0.603	1077.6	−9.9	0.856	475.8	−4.6
0.327	1162.6	−0.4	0.759	761.1	−9.2			
x Dipropylamine + (1 − x) Dipropyl Ether								
0.00551	3.1	1.4	0.160	38.1	−1.6	0.485	79.2	2.3
0.0182	8.0	2.4	0.204	47.3	−0.4	0.598	76.2	−0.8
0.0273	10.4	2.2	0.255	54.1	−1.6	0.760	60.0	−1.6
0.0832	24.2	1.2	0.308	63.1	0.3	0.870	38.8	−0.4
0.0959	26.2	0.1	0.350	68.0	0.5	0.912	30.3	2.3
x Dipropylamine + (1 − x) Tripropylamine								
0.0152	19.4	1.1	0.274	250.1	−1.3	0.524	303.4	−1.8
0.0510	58.4	0.0	0.337	280.5	−0.1	0.554	301.1	−0.7
0.163	172.2	0.9	0.357	290.6	3.1	0.623	288.3	0.6
0.171	179.4	1.2	0.411	302.0	1.3	0.760	234.2	0.2
0.247	231.6	−3.6	0.445	305.4	−0.3	0.905	125.1	−0.0
x Dipropylamine + (1 − x) Dipropyl Sulfide								
0.0625	16.5	−4.0	0.305	102.0	2.1	0.719	102.7	-0.5
0.0963	32.2	0.7	0.386	112.8	−3.3	0.786	86.4	-0.5
0.153	52.2	0.0	0.451	121.4	−2.0	0.837	73.5	2.0
0.195	68.6	1.6	0.537	126.8	1.4	0.882	53.1	-2.4
0.283	95.4	1.2	0.681	112.0	1.5			
x Propane-1-thiol + (1 − x) Dipropyl Ether								
0.0830	34.1	−2.2	0.236	93.6	4.6	0.742	118.1	6.6
0.137	50.1	−3.0	0.323	117.0	3.1	0.782	101.3	0.9
0.170	60.8	−4.9	0.500	132.5	−5.7	0.830	78.9	−5.6
0.191	74.3	0.8	0.633	132.2	0.2			
x Propane-1-thiol + (1 − x) Tripropylamine								
0.156	176.2	-1.4	0.407	388.1	−6.2	0.772	340.0	4.4
0.246	268.9	-1.6	0.570	440.2	4.0	0.856	237.0	−2.1
0.300	326.0	6.8	0.687	395.7	−4.5			
x Propane-1-thiol + (1 − x) Dipropyl Sulfide								
0.0941	-8.2	−0.3	0.347	−13.9	0.4	0.611	−11.7	0.1
0.142	−10.3	0.0	0.400	−14.5	−0.2	0.710	−8.7	0.4
0.197	−12.1	0.2	0.506	−13.7	−0.3	0.876	−3.8	−0.2
0.243	−13.3	0.0						

Table 2. Excess Molar Enthalpies H_m^E for x {$CH_3CH_2CH_2OH$, $(CH_3CH_2CH_2)_2NH$, or $(CH_3CH_2CH_2SH)$} + (1 − x) $(CH_3CH_2CH_2)_2CO$ and the Deviations Δ Calculated from Eq 1 and the Parameters of Table 4

x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$	x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$	x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$
x Propan-1-ol + (1 − x) Heptan-4-one								
0.0481	294.3	2.1	0.323	1122.7	−1.2	0.732	815.2	7.8
0.117	608.2	−18.9	0.350	1140.1	−3.5	0.769	740.2	6.8
0.178	860.1	13.0	0.499	1120.1	−2.3	0.878	451.4	−10.3
0.255	1041.4	8.4	0.581	1035.0	−6.7			
x Dipropylamine + (1 − x) Heptan-4-one								
0.00783	−4.1	−3.7	0.320	91.3	0.0	0.661	154.5	1.2
0.0484	−5.4	−6.6	0.337	97.5	−0.4	0.736	141.4	1.9
0.0727	4.3	−0.4	0.420	124.8	−1.7	0.793	120.5	−0.8
0.113	18.0	4.1	0.489	143.4	−0.7	0.830	104.6	−1.4
0.224	54.3	1.7						
x Propane-1-thiol + (1 − x) Heptan-4-one								
0.0403	7.5	0.2	0.219	33.0	−0.2	0.613	68.2	0.2
0.0862	15.1	0.6	0.426	58.8	−0.1	0.728	59.0	−0.8
0.177	27.1	−0.4	0.478	64.0	0.4	0.848	39.2	0.5

Table 3. Excess Molar Enthalpies H_m^E for x {$(\mathrm{CH_3CH_2CH_2})\mathrm{N}$ or $\mathrm{CH_3CH_2CH_2SH}$} + (1 − x) $\mathrm{C_7H_{16}}$ and the Deviations Δ Calculated from Eq 1 and the Parameters of Table 4

x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$	x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$	x	$H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}})$	$\Delta/(\mathrm{J\cdot mol^{-1}})$
			x Tripropylamine + (1 − x) Heptane					
0.0465	5.5	−0.2	0.198	17.2	0.2	0.555	18.6	0.0
0.0586	6.0	−0.4	0.223	17.7	0.0	0.675	15.1	0.2
0.0854	9.1	0.0	0.242	19.0	0.2	0.742	11.9	0.1
0.132	12.7	0.2	0.355	21.4	−0.3	0.821	7.7	-0.2
0.166	14.9	−0.1	0.449	21.2	−0.1			
			x Propane-1-thiol + (1 − x) Heptane					
0.0900	217.2	7.7	0.320	570.1	16.5	0.644	696.4	−0.4
0.160	326.1	−7.6	0.491	683.8	−17.1	0.670	680.2	1.8
0.191	377.0	−5.0	0.580	724.1	5.1	0.838	417.8	−2.0
0.236	444.3	−2.5	0.601	719.3	4.0	0.869	348.1	0.1

Table 4. Parameters A_r and Standard Deviations σ for the Representation of Molar Excess Enthalpies at 298.15 K by Eq 1

	A_0	A_1	A_2	A_3	$\sigma/(\mathrm{J\cdot mol^{-1}})$
$x\ \mathrm{C_3H_7OH}$					
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{O}$	2960	1206	1066	1187	5
+ (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$	−1131	1355	-855	1127	6
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{S}$	4746	1104	836	1347	10
$x\ (\mathrm{C_3H_7})_2\mathrm{NH}$					
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{O}$	309	-52	23	35	2
+ (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$	1226	67	176	−315	2
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{S}$	502	-31	−80	−120	2
$x\ \mathrm{C_3H_7SH}$					
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{O}$	553	-64	−48	−82	4
+ (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$	1721	−440	-167	29	5
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{S}$	−54	-24	−11	−22	0.2
$x\ \mathrm{C_3H_7OH}$ + (1 − x) $(\mathrm{C_3H_7})_2\mathrm{CO}$	4486	1491	1212	−600	10
$x\ (\mathrm{C_3H_7})_2\mathrm{NH}$+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{CO}$	585	−373	-220	−56	3
$x\ \mathrm{C_3H_7SH}$ + (1 − x) $(\mathrm{C_3H_7})_2\mathrm{CO}$	260	−128	−35	97	1
$x\ (\mathrm{C_3H_7})_3\mathrm{N}$ + (1 − x) $\mathrm{C_7H_{16}}$	81	40	−2	2	0.3
$x\ \mathrm{C_3H_7SH}$ + (1 − x) $\mathrm{C_7H_{16}}$	2820	−856	−73	885	9

systems studied in this work. To each set of experimental values, a polynomial of the type

$$\Delta/(\mathrm{J\cdot mol^{-1}}) = H_\mathrm{m}^\mathrm{E}/(\mathrm{J\cdot mol^{-1}}) - x_i(1 - x_i)\sum_{r=0}^{n} A_r(1 - 2x_i)^r \tag{1}$$

was fitted by the method of unweighted least squares. The coefficients A_r are given in Table 4, and x_i refers to the proton donor. The H_m^E values, used in the Discussion, for x {$\mathrm{C_3H_7OH}$, $(\mathrm{C_3H_7})_2\mathrm{O}$, $(\mathrm{C_3H_7})_2\mathrm{NH}$, or $\mathrm{C_3H_7COC_3H_7}$} + (1 − x) $\mathrm{C_7H_{16}}$ (Oswald *et al.*, 1986; Christensen *et al.*, 1988a,b; Christensen *et al.*, 1982a) and for $x\ (\mathrm{C_3H_7})_2\mathrm{S}$ + (1 − x) $\mathrm{C_6H_{14}}$ (Christensen *et al.*, 1982b) have been reported previously.

$H_{i,\mathrm{m}}^\mathrm{E}(x_i{=}0)$ was determined by applying a polynomial to the reduced excess enthalpy as follows:

$$H_\mathrm{m}^\mathrm{E}/x_1x_2 = a + bx_i + cx_i^2 + ... \tag{2}$$

$H_{i,\mathrm{m}}^\mathrm{E}(x_i{=}0)$ was calculated by extrapolating the individual curves to infinite dilution ($x_1 \rightarrow 0$). A plot of the reduced excess enthalpy as a function of x_1 revealed the range of mole fraction that should be fixed for each system, which was generally in the range $0 < x_i < 0.5$. $H_{i,\mathrm{m}}^\mathrm{E}(x_i{=}0)$ values, as calculated from eq 2, are given in Table 5.

Table 5. Excess Partial Molar Enthalpies at Infinite Dilution, $H_{i,\mathrm{m}}^\mathrm{E}(x_i{=}0)$, Evaluated from the Coefficient a of Eq 2 for all Mixtures Including Uncertainties (in Parentheses)

mixture	$H_{i,\mathrm{m}}^\mathrm{E}(x_i{=}0)/(\mathrm{J\cdot mol^{-1}})$
$x\ \mathrm{C_3H_7OH}$ + (1 − x) $\mathrm{C_7H_{16}}$	25332 (246)
$x\ (\mathrm{C_3H_7})_2\mathrm{NH}$ + (1 − x) $\mathrm{C_7H_{16}}$	2469 (35)
$x\ \mathrm{C_3H_7SH}$ + (1 − x) $\mathrm{C_7H_{16}}$	2718 (144)
$x\ (\mathrm{C_3H_7})_2\mathrm{O}$ + (1 − x) $\mathrm{C_7H_{16}}$	845 (2)
$x\ (\mathrm{C_3H_7})_3\mathrm{N}$ + (1 − x) $\mathrm{C_7H_{16}}$	121 (4)
$x\ (\mathrm{C_3H_7})_2\mathrm{S}$ + (1 − x) $\mathrm{C_6H_{14}}$	1886 (96)
$x\ (\mathrm{C_3H_7})\mathrm{C_2O}$ + (1 − x) $\mathrm{C_7H_{16}}$	4778 (19)
$x\ \mathrm{C_3H_7OH}$	
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{O}$	6226 (50)
+ (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$	807 (116)
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{S}$	7866 (202)
$x\ (\mathrm{C_3H_7})_2\mathrm{NH}$	
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{O}$	471 (32)
+ (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$	1257 (23)
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{S}$	248 (26)
$x\ \mathrm{C_3H_7SH}$	
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{O}$	359 (53)
+ (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$	1131 (95)
+ (1 − x) $(\mathrm{C_3H_7})_2\mathrm{S}$	−115 (3)
$x\ \mathrm{C_3H_7OH}$ + (1 − x) $(\mathrm{C_3H_7})_2\mathrm{CO}$	6600 (129)
$x\ (\mathrm{C_3H_7})_2\mathrm{NH}$ + (1 − x) $(\mathrm{C_3H_7})_2\mathrm{CO}$	−336 (93)
$x\ \mathrm{C_3H_7SH}$ + (1 − x) $(\mathrm{C_3H_7})_2\mathrm{CO}$	200 (3)

Discussion

The experimental values for H_m^E are positive over the whole concentration range for all mixtures except for $x\ \mathrm{C_3H_7OH}$ + (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$ and $x\ \mathrm{C_3H_7SH}$ + (1 − x) $(\mathrm{C_3H_7})_3\mathrm{N}$. The enthalpy change as a result of hydrogen bonding between dissimilar species is masked in most of these mixtures by positive enthalpic effects resulting from dissociation. An interpretation of all the results presented here is possible if one assumes that the overall H_m^E for these mixtures is due to three separate terms (Diogo *et al.*, 1993):

$$H_\mathrm{m}^\mathrm{E} = \Delta H_\mathrm{AH} + \Delta H_\mathrm{B} + \Delta H_\text{H-bond} \tag{3}$$

where H_m^E is the heat of mixing for a hydrogen donor (AH) with a hydrogen acceptor (B), ΔH_AH accounts for a positive contribution due to the breakdown of bonds between hydrogen donor molecules, ΔH_B corresponds to a positive contribution due to the breakdown of bonds between hydrogen acceptor molecules, and $\Delta H_\text{H-bond}$ involves a negative contribution due to the association of AH and B molecules. The small enthalpic contribution (positive or negative) due to B···B reorganization, caused by the entry of AH, is neglected in this model.

Extending the technique of the use of $H_\mathrm{i,m}^\mathrm{E}(x_i{=}0)$ to describe hydrogen bond strengths (Stokes *et al.*, 1975; Van Ness *et al.*, 1967; Woycicka *et al.*, 1972), a measure of the self-association between molecules of AH and a measure of the self-association between molecules of B can be obtained from $H_\mathrm{AH,m}^\mathrm{E}(x_\mathrm{AH}{=}0)$[AH+hydrocarbon] and $H_\mathrm{B,m}^\mathrm{E}(x_\mathrm{B}{=}0)$[B+hydrocarbon], respectively. Similarly, a measure of the AH···B interaction is obtained by a comparison of the sum of $H_\mathrm{AH,m}^\mathrm{E}(x_\mathrm{AH}{=}0)$[AH+hydrocarbon] and $H_\mathrm{B,m}^\mathrm{E}(x_\mathrm{B}{=}0)$[B+hydrocarbon] with $H_\mathrm{AH,m}^\mathrm{E}(x_\mathrm{AH}{=}0)$[AH+B]. Thus, from eq 3 the hydrogen bond interaction energy ($\Delta H_\text{H-bond}$) can be calculated from

$$\Delta H'_{\text{H-bond}}[\text{AH}\cdots\text{B}] = H^{E}_{\text{AH,m}}(x_{\text{AH}}=0)[\text{AH}\cdots\text{B}] - H^{E}_{\text{AH,m}}(x_{\text{AH}}=0)[\text{AH+hydrocarbon}] - H^{E}_{\text{B,m}}(x_{\text{B}}=0)[\text{B+hydrocarbon}] \quad (4)$$

where $\Delta H'$ refers to the enthalpy change at infinite dilution. The results are reported in Table 6.

Table 5 shows that the hydrogen bonding enthalpy for propan-1-ol self-association, obtained from $H^{E}_{C_3H_7OH}$ -($x_{C_3H_7OH}$=0)[xC$_3$H$_7$OH+(1−x)C$_7$H$_{16}$], was calculated to be (−24.65 ± 0.25) kJ·mol^{-1}. This result compares well with the hydrogen bond enthalpies for alcohols obtained by Funke *et al.* (1989) using the extended real associated solution (ERAS) model (−25.1 kJ·mol^{-1}). Using partial molar enthalpies at infinite dilution, Van Ness *et al.* (1967) and Wóycicka *et al.* (1972) estimate the alcohol self-association to be (−24.2 ± 0.4) and −23.4 kJ·mol^{-1}, respectively. The dipropylamine self-association enthalpy was evaluated to be −2.47 kJ·mol^{-1}. This was far lower than the diethylamine self-association energy estimated by both Funke *et al.* (1989) (−8.5 kJ·mol^{-1}) using ERAS and Cibulka *et al.* (1988) (−10.3 kJ·mol^{-1}), who based his estimate on regression of vapor pressures and liquid molar volumes. The propane-1-thiol self-association enthalpy was calculated to be −2.72 kJ·mol^{-1}.

The hydrogen bond enthalpies for all the examined systems are found in Table 6. It shows that the order of hydrogen bond strengths for systems involving −OH as the proton donor, as defined in terms of enthalpies of interaction ($\Delta H'_{\text{H-bond}}$), is OH···N > OH···O > OH···S. Our *ab initio* results (Bricknell *et al.*, 1995) (gas phase) suggest the same trend, i.e., the proton accepting ability of the atoms under consideration being in the order N > O > S for all proton donors. However, for the liquid phase systems involving −NH or −SH as proton donors, the proton-accepting ability of atoms under consideration is in the opposite order, i.e., S > O > N.

This anomaly may be due to the fact that the formation of a hydrogen bond in the liquid phase is "greatly affected by the interference of neighbouring (propyl) groups, which reduce the available surface area that one atom (proton acceptor) is offering to the other" (Perez-Casas *et al.*, 1991). Bondi (1964) confirms that the functional group contributions to the van der Waals surface area for compounds such as used in this work are, in decreasing order, S > O > N. This is identical to the results obtained for the calculation of $\Delta H'_{\text{H-bond}}$ when −NH or −SH is used as the proton donor, and may explain the hydrogen bond strength order when a relatively weak hydrogen donor (−NH or −SH) is involved in hydrogen bonding.

This hypothesis was tested using heptan-4-one as a proton acceptor, for which the oxygen atom is more exposed than in the ether molecule, and where the C═O group has roughly the same surface area as does the −S− group (Bondi,1964). Results using the oxygen in heptan-4-one as the proton acceptor show that the order of of bond strength of the interactions NH···O or SH···O > NH···S or SH···S (see Table 6). This is opposite to the result for hydrogen bonding using the oxygen in dipropyl ether and supports the concept that the available surface area of the proton acceptor is the dominant factor in determining the relative strengths of hydrogen bonding. This result (that O is a better proton acceptor than S) mirrors the results found using *ab initio* values and also the results obtained for the mixtures when −OH was used as the proton donor in the liquid phase (see Table 6).

Table 6. Hydrogen Bond Interaction Energy, $\Delta H'_{\text{H-bond}}$, from Eq 5

system	$\Delta H'_{\text{H-bond}}$/kJ·mol^{-1}	system	$\Delta H'_{\text{H-bond}}$/kJ·mol^{-1}
−OH···N	−24.65 ± 0.25	−NH···S	−4.11 ± 0.10
−OH···O	−19.95 ± 0.25	−NH···O═C	−7.61 ± 0.09
−OH···S	−19.35 ± 0.25	−SH···N	−1.71 ± 0.14
−OH···O═C	−23.51 ± 0.25	−SH···O	−3.20 ± 0.14
−NH···N	−1.33 ± 0.12	−SH···S	−4.72 ± 0.14
−NH···O	−2.84 ± 0.05	−SH···O═C	−7.30 ± 0.14

[a] Key: −OH = propan-1-ol, −NH = di-*n*-propylamine, −SH = propanethiol, N = tri-*n*-propylamine, O = di-*n*-propyl ether, S = di-*n*-propyl sulfide, O═C = heptan-4-one.

It is possible that the difference in the order of the bond strength of interactions between hydrogen bonds formed with ketones and ethers as proton acceptors is due to the unlike character of the O atoms. Inarrea *et al.* (1988), however, concluded from their results that the different behavior of alkanols in each non-alkanol component is mainly due to the dipole−dipole interactions and that the unlike character of the O atoms in ketone and ether seemingly plays a less important role.

All the molecular complexes examined in this work will also later be evaluated using the ERAS model.

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