

Enthalpies of hydrogen-bonded butylamine-chloroform complexes[†]

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Abstract. Enthalpies of mixing of isomeric butylamine with chloroform were determined at 30°C by a Calvet-type microcalorimeter. The system showed highly exothermic behaviour due to hydrogen-bonded complex formation on mixing. The enthalpies of complex formation were calculated by means of a thermo-chemical cycle and the values vary from 1-aminobutane to 2-amino-2-propane complexes.

Keywords. calorimetry; amine-chloroform complexes; binary systems; enthalpy of complex.

1. Introduction

The energies of hydrogen-bonded complexes depend on the electron densities of proton-acceptor and -donor atoms of the H-bond forming molecules. Steric and electromeric effects also play important roles in strengthening or weakening the H-bond (Geisler *et al* 1971). The enthalpies of H-bonded complexes therefore depend on the functional groups as well as the structure of complex-forming molecules. In our earlier work we have determined the enthalpies of H-bonded complexes between $\text{NH}_2 \dots \text{OH}$, $\text{NH} \dots \text{OH}$, $\text{N} \dots \text{OH}$ groups and also studied the isomeric effect on the strengths of H-bonds (Pradhan and Mathur 1979; Pradhan 1981; Pradhan and Pathak 1986). In the present communication the work on the enthalpies of complex formation between isomeric butylamines and chloroform has been reported.

2. Experimental

The isomeric butylamines (S.D. Chemicals, AR grade) were purified by fractional distillation and the chloroform (S.D. Chemicals, AR grade) was purified by the standard method (Riddick and Bunger 1970). All the compounds were dried over freshly activated molecular sieves. The heats of mixing were determined by heat flux Calvet microcalorimeter (C-80 Setaram model) at 30°C.

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3. Results and discussion

The enthalpies of mixing of 1-aminobutane, 1-amino-2-methyl propane, 2-aminobutane and 2-amino-2-methyl propane with chloroform have been given in table 1. The values have been rounded to tens of joules. The data is fitted by means of the least square method in a Redlich-Kister equation:

$$\Delta H = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + E(x_1 - x_2)^3]. \quad (1)$$

The Redlich-Kister parameters along with the standard deviations have been given in table 2. The enthalpies of mixing as a function of mole fraction of amine have been represented in figure 1.

All the four systems exhibit highly exothermic characteristics due to the formation of hydrogen-bonded complexes between the amine and chloroform molecules as shown in figure 2.

The enthalpies of complex formation have been calculated by means of a thermochemical cycle (Murakami and Fujishiro 1966). The ultimate equation from the cycle is

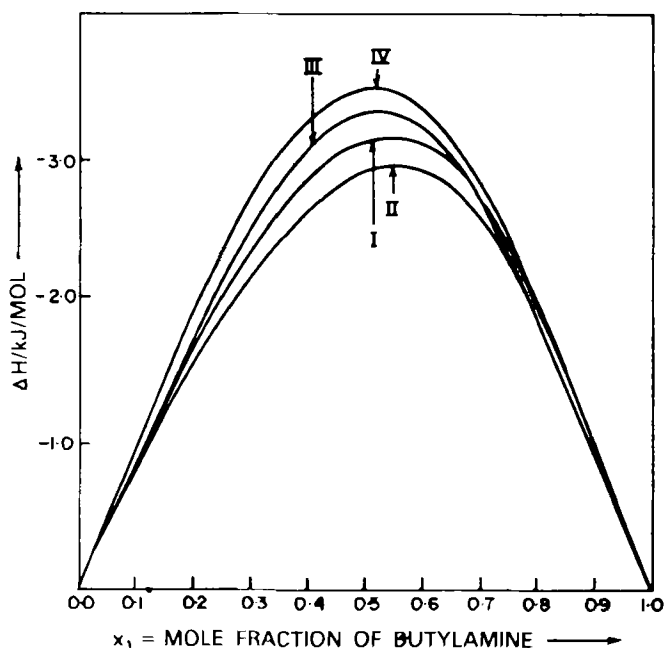
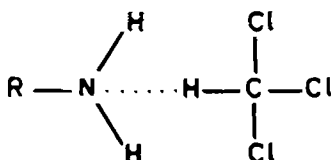
$$\Delta H_c = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d, \quad (2)$$

Table 1. The enthalpies of mixing of isomeric butylamine (1)-chloroform (2) systems at 30°C.

(mole fraction of amine)	ΔH (J/mole)	x_1 (mole fraction of amine)	ΔH (J/mole)
1-Aminobutane (1) + chloroform (2)		2-Aminobutane (1) + chloroform (2)	
0.0898	-820	0.0909	-800
0.2056	-1770	0.1577	-1420
0.3030	-2350	0.2678	-2270
0.4000	-2830	0.2908	-2470
0.4963	-3140	0.3269	-2710
0.5908	-3130	0.4700	-3290
0.6718	-2850	0.5192	-3320
0.7007	-2680	0.5985	-3210
0.7959	-2000	0.7007	-2690
0.9074	-940	0.7397	-2420
		0.8000	-1870
		0.8565	-1340
		0.9026	-880
1-Amino-2-methylpropane (1) + chloroform (2)		2-Amino-2-methyl propane (1) + chloroform (2)	
0.1008	-890	0.0782	-800
0.2000	-1590	0.1977	-1950
0.3110	-2210	0.3052	-2780
0.3965	-2660	0.3082	-2790
0.5001	-2920	0.4058	-3280
0.5837	-2920	0.4827	-3470
0.6647	-2700	0.5438	-3440
0.7364	-2350	0.6058	-3290
0.7919	-1920	0.7031	-2800
0.8000	-1880	0.8148	-1870
0.8125	-1800	0.9078	-890
0.8618	-1320		
0.8837	-1140		
0.9025	-910		

Table 2. The Redlick-Kister parameters for enthalpies of mixing of isomeric butylamine(1) - chloroform(2) systems at 30°C.

System	<i>B</i> (J/mole)	<i>C</i> (J/mole)	<i>D</i> (J/mole)	<i>E</i> (J/mole)	Standard deviation (J/mole)
1-Aminobutane + CHCl ₃	-12498.9	-2422.5	2825.1	2672.4	21
1-Amino-2-methyl propane + CHCl ₃	-11639.7	-2846.0	2244.7	3686.9	18
2-Aminobutane + CHCl ₃	-13280.1	-1301.6	5207.4	1848.6	13
2-Amino-2-methyl propane + CHCl ₃	-13913.3	-716.4	4377.6	1581.4	12

**Figure 1.** ΔH vs. x_1 plots for isomeric butylamine (1)-chloroform (2) systems. I-1-amino butane; II-1-amino-2-methyl propane; III-2-aminobutane; IV-2-amino-2-methyl propane.**Figure 2.** The amino-chloroform hydrogen-bonded complex.

where ΔH_c is the enthalpy of complex formation, ΔH_1 and ΔH_2 are respectively the partial molar enthalpies of amine and chloroform in a non-polar solvent i.e. *n*-hexane, ΔH_3 is the partial molar enthalpy of mixing of amine in chloroform and ΔH_4^d is the dipolar stabilisation energy of the complex.

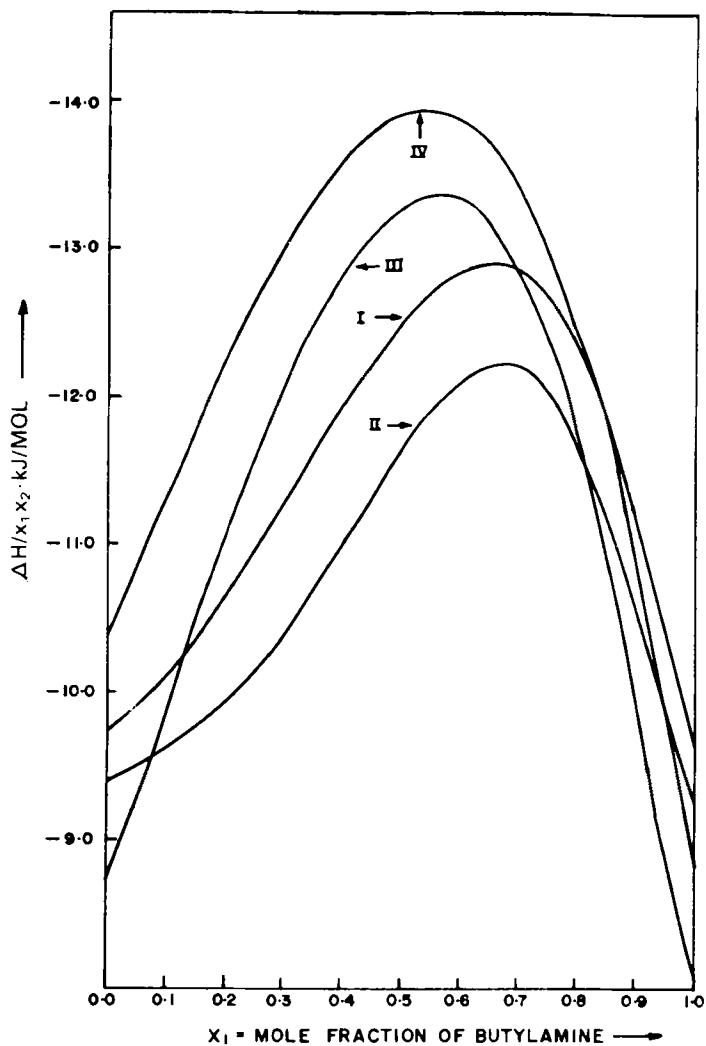


Figure 3. $\Delta H_1/x_1x_2$ vs. x_1 plots for isomeric butylamine (1)-chloroform (2) systems. I-1-aminobutane; II-1-amino-2-methyl propane; III-2-aminobutane; IV-2-amino-2-methyl propane.

The ΔH_1^d is the difference between the dipolar stabilisation enthalpies of the complex in non-polar (*n*-hexane) and polar (chloroform) media.

The dipolar stabilisation enthalpy of a dipole in medium 'i' is calculated from the free energy of dipole stabilisation, which is given by (Buttcher 1952)

$$\Delta G_i = -1/2 f \cdot \mu^2 (1 - \alpha f), \quad (3)$$

the value of f is given by the expression

$$f = 2(\epsilon - 1)/a^3 (2\epsilon + 1), \quad (4)$$

where ' ϵ ' is the dielectric constant ' a ' is the radius and ' α ' is molecular polarizability.

The values of ΔH_1 are taken from our previous work (Pradhan and Mathur

Table 3. The enthalpies of complex formations of isomeric butylamine-chloroform complexes calculated by (2).

System	ΔH_1 (kJ/mole)	ΔH_2 (kJ/mole)	ΔH_3 (kJ/mole)	ΔH_4^d (kJ/mole)	ΔH_c (kJ/mole)
1-Aminobutane- <i>n</i> -hexane	8.4 ± 0.3	-	-	-	-
1-Amino-2-methylpropane- <i>n</i> -hexane	7.5 ± 0.3	-	-	-	-
2-Aminobutane- <i>n</i> -hexane	6.6 ± 0.3	-	-	-	-
2-Amino-2-methylpropane- <i>n</i> -hexane	4.9 ± 0.3	-	-	-	-
Chloroform- <i>c</i> -hexane		2.6 ± 0.05			
1-Aminobutane-chloroform			-9.7 ± 0.1	1.2	-19.5 ± 0.5
1-Amino-2-methylpropane-chloroform			-9.4 ± 0.1	1.2	-18.3 ± 0.5
2-Aminobutane-chloroform			-8.7 ± 0.1	1.2	-16.7 ± 0.5
2-Amino-2-methylpropane-chloroform			-10.3 ± 0.1	1.2	-16.6 ± 0.5

1978), while the ΔH_2 value is obtained from the literature data on heats of mixing of chloroform which *c*-hexane (Nagata *et al* 1980).

The ΔH_3 values are obtained from the extrapolation of $\Delta H/x_1x_2$ vs. x_1 curves to zero mole fraction of amine. The ΔH values at different mole fractions of amine (x_1) were obtained from the Redlick-Kister equation (1) and the $\Delta H/x_1x_2$ vs. x_1 curves are represented in figure 3.

The values of ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4^d and the ultimate values of enthalpies of amine-chloroform complex formation are given in table 3. The enthalpies of complex formation between the isomeric amine-chloroform changes in the order-

n-amine > iso-amine > sec-amine > tert-amine

Our previous work on amine-alcohol complex formation indicated that a complex between a tertiary and a normal molecule is slightly stronger than that between two normal molecules due to the electromeric effect of CH_3 groups on the α carbon atom. However, we have also found that when two tertiary molecules interact, the strength of H-bonded complexes decreases due to the dominance of the steric effect. In the presently studied systems, the tertiary amine-chloroform complexes are weaker by about 3 kJ/mole as compared to normal amine-chloroform complexes. It seems therefore that there is a steric repulsion between the CH_3 groups of a tertiary molecule and the three chlorine atoms of chloroform and the system behaves like a two-tertiary molecular system.

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