

Enthalpies of complex formation of dibutyl and tributyl amines with isomeric butanols†

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Abstract. Enthalpies of complex formation (ΔH_c) of dibutyl and tributyl amines with the four isomeric butanols were determined at 30°C. The present data were compared with the previous data on isomeric butanols with monobutyl amine complexes. The ΔH_c in the case of *n*-alcohol has been found to decrease by about 4.0 ± 0.4 kJ/mole on replacement of each hydrogen atom of the NH_2 group. The branching of the butyl chain, also, decreases the strength of the complex due to steric hindrance.

Keywords. Calorimetry; amine-alcohol interactions; isomeric effect; steric effect; enthalpy of complexes.

1. Introduction

The study of interactions between associated liquids is of considerable academic and practical interest. In earlier work in this series we have reported the study of isomeric and steric effects of primary alcohols and amines on their intermolecular interactions (Pradhan and Pathak 1980a, b, 1984). The present investigation deals with the study of interactions between the molecules of dibutyl amine and tributyl amine with those of isomeric butanols. A comparison of the values of enthalpy of complex formation between dibutyl and tributylamines with isomeric butanol helps us in understanding the effect of the hydrogen atoms of the NH_2 group on the hydrogen bonded complexes, as well as the isomeric effect on the intermolecular interactions.

2. Experimental

n-Hexane (SD Chemicals, AR), isomeric butanols (BDH, AR), *n*-butyl amine, dibutyl amine and tributylamine (Fluka) were purified by fractional distillation. All the compounds were dried over freshly activated molecular sieves.

A 1:1 Complex of each system was prepared by making an equimolar mixture of amine and alcohol. The enthalpies of mixing of these complexes with *n*-hexane were measured at concentrations below the 0.05 mole fraction of the complex at 30°C using the dewar type calorimeter. Experimental details are given in an earlier communication (Pradhan and Pathak 1980).

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3. Results and discussion

The enthalpies of mixing of butanols-dibutyl amine and butanols-tributyl amine complexes with *n*-hexane have been reported in table 1. All the systems show endothermic behaviour due to the breaking of hydrogen bonded complexes. The partial molar enthalpies of the complex may therefore be taken as the enthalpy of complex formation (Savini *et al* 1965). The plot of $\Delta H/x_1x_2$ versus mole fraction of the complex (x_1) for dibutyl amine and tributyl amine complexes are presented in figures 1 and 2 respectively.

The enthalpies of complex formation obtained by extrapolating the $\Delta H/x_1x_2$ versus x_1 curves to infinite dilution ($x_1 \rightarrow 0$) for these systems are reported in table 2 along with the values for isomeric butanol-monobutyl amine systems for ready comparison. It may be observed from table 2 that in all the systems containing the isomers of alcohol,

Table 1. Enthalpies of mixing of butanol-dibutylamine and butanol-tributylamine complexes with *n*-hexane at 30°C.

Alcohol	Dibutylamine			Tributylamine			
	X_1	ΔH (J/mole)	$\Delta H/x_1x_2$ (kJ/mol)	X_1	ΔH (J/mole)	$\Delta H/x_1x_2$ (kJ/mol)	
<i>n</i> -BuOH	0.0018	62 ± 0.5	34.5 ± 0.3	0.0014	42 ± 0.5	30.0 ± 0.3	
	0.0020	65 ± 0.5	32.6 ± 0.2	0.0021	58 ± 0.5	27.7 ± 0.2	
	0.0042	123 ± 0.5	29.4 ± 0.1	0.0029	76 ± 0.5	26.3 ± 0.2	
	0.0048	139 ± 0.5	29.1 ± 0.1	0.0048	109 ± 0.5	22.8 ± 0.1	
	0.0080	189 ± 1.0	23.8 ± 0.1	0.0095	183 ± 1.0	19.4 ± 0.1	
	0.0095	211 ± 1.0	22.4 ± 0.1	0.0141	238 ± 1.0	17.1 ± 0.1	
	0.0102	219 ± 1.0	21.7 ± 0.1	0.0147	236 ± 1.0	16.3 ± 0.1	
	0.0201	332 ± 1.0	16.9 ± 0.1	0.0366	371 ± 2.0	10.5 ± 0.2	
	<i>iso</i> -BuOH	0.0024	74 ± 0.5	30.9 ± 0.3	0.0014	39 ± 0.5	27.9 ± 0.3
		0.0048	140 ± 0.5	29.3 ± 0.2	0.0028	73 ± 0.5	26.2 ± 0.2
0.0080		207 ± 1.0	26.1 ± 0.1	0.0051	126 ± 1.0	24.8 ± 0.2	
0.0106		257 ± 1.0	24.5 ± 0.1	0.0094	202 ± 1.0	21.7 ± 0.1	
0.0137		300 ± 1.0	22.2 ± 0.1	0.0134	252 ± 1.0	19.1 ± 0.1	
0.0190		371 ± 2.0	19.9 ± 0.1	0.0180	289 ± 1.0	16.3 ± 0.1	
<i>sec</i> -BuOH	0.0015	48 ± 0.5	32.1 ± 0.3	0.0021	59 ± 0.5	28.2 ± 0.3	
	0.0045	126 ± 0.5	28.1 ± 0.2	0.0030	80 ± 0.5	26.7 ± 0.3	
	0.0097	235 ± 1.0	24.5 ± 0.2	0.0051	128 ± 1.0	25.2 ± 0.2	
	0.0124	270 ± 1.0	22.0 ± 0.1	0.0064	151 ± 1.0	23.7 ± 0.2	
	0.0184	334 ± 1.0	18.2 ± 0.1	0.0099	212 ± 1.0	21.6 ± 0.1	
	0.0224	389 ± 2.0	17.8 ± 0.1	0.0137	254 ± 1.0	18.8 ± 0.1	
	0.0337	466 ± 2.0	14.3 ± 0.1	0.0190	314 ± 1.0	16.9 ± 0.1	
	0.0515	541 ± 2.0	11.1 ± 0.1	0.0302	411 ± 2.0	14.4 ± 0.1	
	<i>tert</i> -BuOH	0.0024	75 ± 0.5	31.3 ± 0.3	0.0018	50 ± 0.5	27.9 ± 0.3
0.0052		146 ± 1.0	28.2 ± 0.3	0.0054	134 ± 0.5	24.9 ± 0.3	
0.0098		242 ± 1.0	24.9 ± 0.2	0.0099	218 ± 1.0	22.2 ± 0.2	
0.0125		280 ± 1.0	22.7 ± 0.2	0.0162	305 ± 1.0	19.1 ± 0.2	
0.0156		340 ± 1.0	22.1 ± 0.1	0.0262	362 ± 1.0	14.2 ± 0.1	
0.0173		350 ± 1.0	20.6 ± 0.1	0.0412	475 ± 2.0	12.0 ± 0.1	
0.0293		534 ± 2.0	18.9 ± 0.1				
0.0439		640 ± 2.0	14.3 ± 0.1				

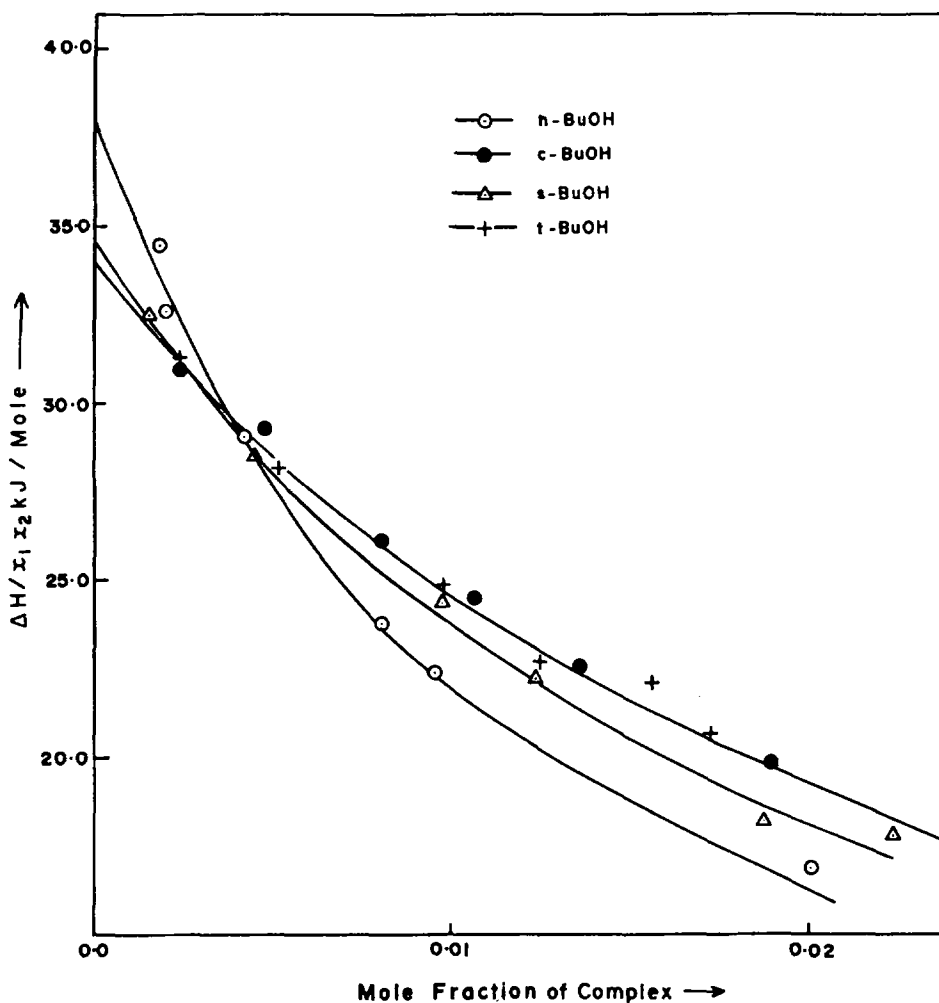


Figure 1. $\Delta H/x_1x_2$ versus mole fraction of the complex (x_1) for dibutyl amine complexes.

the enthalpy of complex formation decreases as

monobutyl amine > dibutylamine > tributyl amine.

Huyskins *et al* (1960) and Lambert *et al* (1963) from their studies on *n*-butyl amine-*n*-butanol system by NMR calorimetry and conductivity have concluded that *n*-butyl amine and *n*-butanol form a non-linear 1:1 type complex. The nitrogen of the NH_2 group is hydrogen bonded with the H of the OH of alcohol. The two hydrogen atoms of NH_2 group form two weak hydrogen bonds with the O of the OH group. The results of the present work support the Huyskins model of the complex, as the enthalpy of complex formation decreases by about 4.0 ± 0.4 kJ/mole on replacement of each hydrogen atom of the NH_2 group. It is seen from the tributyl amine-*n*-butanol complex that the strength of the $\text{N} \cdots \text{H}$ bond is about 35 ± 0.4 kJ/mole and the strength of the $\text{N}-\text{H} \cdots \text{O}-\text{H}$ bond is about 38.4 ± 0.4 kJ/mole.

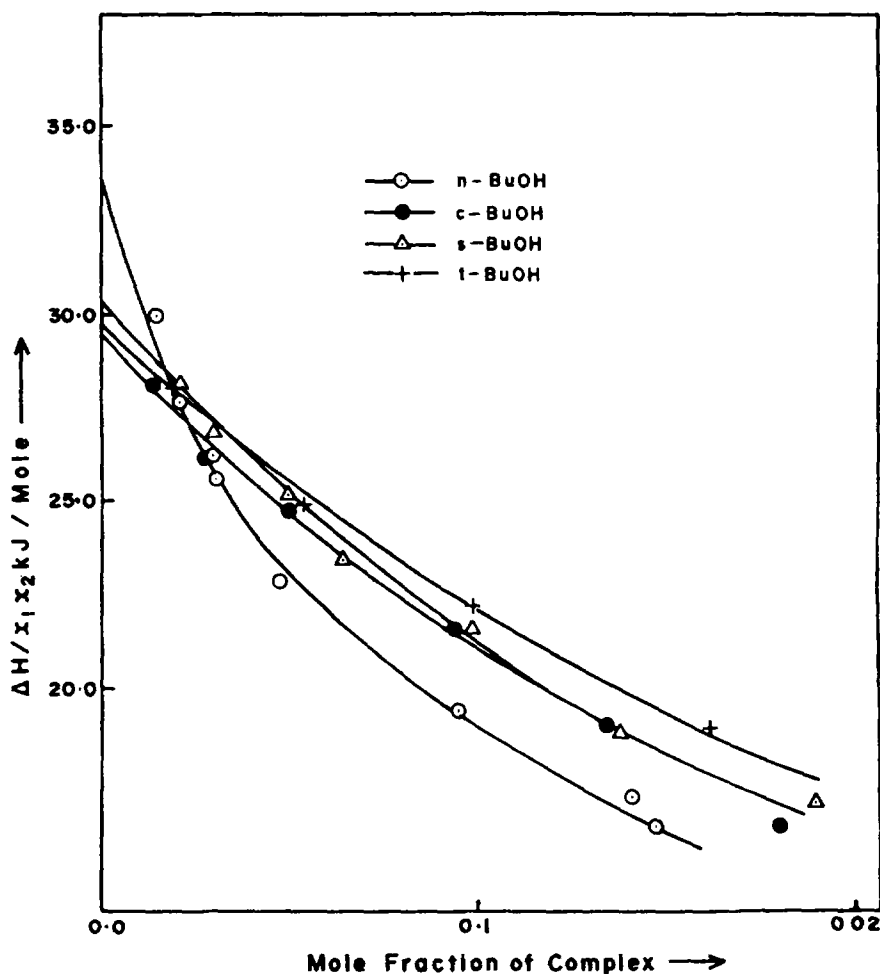


Figure 2. $\Delta H/x_1 x_2$ versus mole fraction of the complex (x_1) for tributyl amine complexes.

Table 2. Enthalpies of mixing of 1:1 complexes of isomeric butanols with monobutyl amine, dibutyl amine and tributyl amine.

Alcohol	Monobutyl amine (kJ/mole)	Dibutyl amine (kJ/mole)	Tributyl amine (kJ/mole)
<i>n</i> -BuOH	-42.7 ± 0.4	-38.4 ± 0.4	-34.8 ± 0.4
<i>iso</i> -BuOH	-41.9 ± 0.4	-34.5 ± 0.4	-29.5 ± 0.4
<i>sec</i> -BuOH	-40.9 ± 0.4	-34.5 ± 0.4	-29.5 ± 0.4
<i>tert</i> -BuOH	-43.1 ± 0.4	-34.0 ± 0.4	-29.8 ± 0.4

For all the branched isomers of alcohols the enthalpy of complex formation with dibutyl amine is about 34.5 ± 0.5 kJ/mole. The decrease in the strength of the complex by about 4.0 kJ/mole compared to normal alcohol complex may be attributed to the steric hindrance caused by the CH_3 group on the *iso*-, *sec*- and *tert*-molecules. It may

also be noted that the enthalpy of complex formation between the branched chain alcohol and dibutyl amine is nearly equal to that between tributyl amine and the normal alcohol. In the latter case there is no H atom on the amino group to form the weak hydrogen bond with the oxygen of alcohol. It seems therefore that in the case of diamine and isomeric alcohol, the weak hydrogen bond formation between the H of the NH group and the O of the OH group does not take place because of the steric repulsion by the CH₃ group present on the alcohol skeleton.

The steric effect is also apparent in the case of branched alcohol and tri-butylamine complexes. The enthalpy of complex formation of these is lowest amongst the series and is of the order of 29.7 ± 0.3 kJ/mole.

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