

Calorimetric study of isomeric and steric effects amine-alcohol interactions

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Abstract. The enthalpy of complex formation between different isomers of butylamine and butylalcohol was determined at 30°C by obtaining the partial molar enthalpy of dissociation of 1:1 complexes in *n*-hexane. In both series *viz.* normal amine with isomeric alcohols and normal alcohol with isomeric amines, the enthalpy of complex formation showed the same trend as $t > n > iso > sec$.

The trend in normal-normal, normal-tertiary, tertiary-tertiary and secondary-secondary complexes was as $t-n > n-n > t-t > sec-sec$. Both these trends were explained in terms of steric and electromeric effects.

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

1. Introduction

Variation in physical properties depend on the position at which the alkyl chain is branched and the nature of the substituted group. Branching has two effects *viz* a steric effect which depends on the geometry of the substituted group and the isomeric effect (inductive $+I$ or $-I$ effect) which depends on the nature of the group. In the present investigation we have determined the enthalpies of complex formation between different isomers of butyl amine and butanols by dissociation method (Pradhan and Pathak 1980). The comparison of the calorimetric data thus obtained helps in understanding the effect of steric hindrance and induction on the molecular interactions between these compounds.

2. Experimental

The compounds used in the present investigation and the methods of their purification have already been given earlier (Pradhan and Mathur 1979). The heats of mixing were determined at 30°C by a calorimeter specially constructed for this purpose. The experimental details and the accuracy have been given earlier (Pradhan and Pathak 1980).

3. Results and discussion

Heats of mixing data for nine systems consisting of *n*-hexane with synthetically prepared 1:1 complexes of *n*-BuNH₂ + *n*-BuOH, *n*-BuNH₂ + iso-BuOH, *n*-BuNH₂ +

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Table 1. Heats of mixing of 1:1 complexes of isomeric butylamines and isomeric butanols with *n*-hexane at 30°C.

X_1 Mole fraction complex	ΔH (J/mol)	$\Delta H/x_1x_2$ (kJ/mol)	X_1 Mole fraction complex	ΔH (J/mol)	$\Delta H/x_1x_2$ (kJ/mol)
<i>n</i> -BuNH ₂ : <i>n</i> -BuOH					
0-0011	45	40.9	0-0040	137	34.4
0-0013	51	39.3	0-0059	187	31.9
0-0025	93	38.0	0-0087	245	28.4
0-0035	126	36.1	0-0099	262	26.7
0-0051	169	33.3	0-0123	302	24.8
0-0079	241	30.7	0-0139	325	23.7
0-0109	295	27.4	0-0216	425	20.1
0-0175	409	23.8	0-0431	628	15.2
0-0266	543	21.0	<i>n</i> -BuOH: <i>s</i> -BuNH ₂		
0-0403	673	17.4	0-0010	39	39.0
<i>n</i> -BuNH ₂ : <i>i</i> -BuOH					
0-0012	46	38.4	0-0029	103	35.6
0-0025	87	34.9	0-0062	200	32.4
0-0051	152	30.0	0-0105	278	26.7
0-0076	204	27.0	0-0150	341	23.1
0-0110	260	23.9	0-0200	386	20.7
0-0147	325	22.4	0-0258	472	18.8
0-0193	395	20.9	<i>n</i> -BuOH: <i>t</i> -BuNH ₂		
0-0322	593	17.3	0-0012	51	42.5
<i>n</i> -BuNH ₂ : <i>s</i> -BuOH					
0-0011	40	36.8	0-00136	57	41.9
0-0023	78	34.1	0-0036	136	38.5
0-0035	109	31.2	0-0051	188	37.0
0-0041	119	29.1	0-0058	204	35.5
0-0072	191	25.7	0-0067	223	33.5
0-0122	285	23.7	0-0081	264	32.8
0-0179	378	21.5	0-0110	314	28.9
0-0244	464	19.5	0-0216	503	23.8
0-0319	564	18.3	0-0288	587	21.0
<i>n</i> -BuNH ₂ : <i>t</i> -BuOH					
0-00175	69	39.5	0-0378	692	19.0
0-0021	82	39.1	<i>s</i> -BuOH: <i>S</i> -BuNH ₂		
0-00285	106	37.3	0-0020	68	33.9
0-0039	140	36.0	0-0036	118	32.9
0-0060	203	34.0	0-0057	179	31.6
0-0085	267	31.7	0-0084	253	30.3
0-0117	346	29.9	0-0118	339	29.1
0-0165	443	27.3	0-0141	886	27.7
0-0210	520	25.3	0-0174	449	26.3
0-0278	620	23.0	0-0220	524	24.4
<i>n</i> -BuOH: <i>i</i> -BuNH ₂					
0-00106	41.5	39.2	<i>t</i> -BuOH: <i>t</i> -BuNH ₂		
0-00112	44.0	39.3	0-00137	48.8	35.6
0-0021	80	38.1	0-0023	80	34.8
0-0021	77	36.8	0-0044	145	33.0
			0-0070	217	31.2
			0-0090	268	30.0
			0-0132	351	27.0
			0-0190	467	25.0
			0-0277	587	21.8

n-BuOH, *n*-BuNH₂ + sec. -BuOH, *n*-BuOH + iso-BuNH₂, *n*-BuOH + sec. BuNH₂, *n*-BuOH + *t*-BuNH₂, sec. BuOH + Sec. BuNH₂, *t*-BuOH + *t*-BuNH₂ are given in table 1. The $\Delta H/x_1x_2$ values have been fitted in an equation of the type

$$\Delta H/x_1x_2 = A + Bx_1 + Cx_1^2 + \dots$$

and the values of the constants are given in table 2 along with the standard deviation. The values of the enthalpy of complex formation rounded to the first decimal are given in table 3.

The enthalpy of complex formation of amines with *n*-butanol and that of butanols with *n*-butylamine shows a similar trend which is tertiary > normal > iso- > sec. In both alcohol and amine the tertiary molecule has the lowest enthalpy of self-association among the four isomers. Whereas the enthalpy of complex formation between the tertiary amine and *n*-butanol or tertiary butanol and *n*-butyl amine is higher than that between *n*-butanol and *n*-butyl amine. This reversal in the trend may be explained in terms of isomeric and steric effects.

At α -carbon atom the tertiary molecule has three methyl groups which increases the charge density on N or O atom (+I effect) (Geisler *et al* 1971) and favours the hydrogen bond formation. Also the methyl groups make the molecule bulkier and introduces a steric hindrance when it interacts with other molecule.

In interaction between the tertiary and normal isomer, the steric hindrance is small as the latter does not possess the protruding methyl group. So the higher enthalpy of

Table 2. Least square constants for the equation $\Delta H/x_1x_2 = A + Bx_1 + Cx_1^2 \dots$

System	A	B ($\times 10^2$)	C ($\times 10^3$)	D ($\times 10^5$)	E ($\times 10^6$)	STD
<i>n</i> -BuNH ₂ : <i>n</i> -BuOH	42.66	-21.83	92.874	-19.655	15.370	0.34
<i>n</i> -BuNH ₂ : <i>i</i> -BuOH	41.91	-32.37	20.971	-65.505	75.229	0.11
<i>n</i> -BuNH ₂ : <i>s</i> -BuOH	40.71	-37.34	30.446	-11.294	14.825	0.36
<i>n</i> -BuNH ₂ : <i>t</i> -BuOH	43.06	-23.25	16.597	-66.019	97.379	0.17
<i>n</i> -BuOH: <i>i</i> -BuNH ₂	41.38	-19.28	50.122	-14.366	-71.512	0.31
<i>n</i> -BuOH: <i>s</i> -BuNH ₂	40.04	-12.75	-25.151	32.822	-63.084	0.33
<i>n</i> -BuOH: <i>t</i> -BuNH ₂	44.78	-19.76	63.824	-93.107	-38.982	0.42
<i>s</i> -BuOH: <i>s</i> -BuNH ₂	35.77	-10.63	82.767	-46.266	90.573	0.10
<i>t</i> -BuOH: <i>t</i> -BuNH ₂	36.49	-67.10	-29.059	27.339	-54.194	0.14

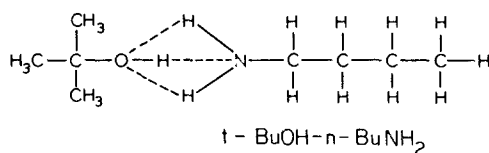
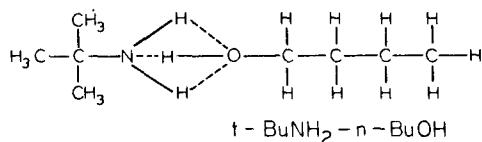
STD-Standard deviation.

Table 3. Enthalpy of complex formation of different isomeric butylamine-butyl alcohol 1:1 complexes.

Complex	$\Delta H (\pm 0.2)$ (kJ/mol)	Complex	$\Delta H (t 0.2)$ (kJ/mol)
<i>n</i> -BuNH ₂ : <i>n</i> -BuOH	42.7	<i>n</i> -BuOH: <i>n</i> -BuNH ₂	42.7
<i>n</i> -BuNH ₂ : <i>i</i> -BuOH	41.9	<i>n</i> -BuOH: <i>i</i> -BuNH ₂	41.4
<i>n</i> -BuNH ₂ : <i>s</i> -BuOH	40.7	<i>n</i> -BuOH: <i>s</i> -BuNH ₂	40.0
<i>n</i> -BuNH ₂ : <i>t</i> -BuOH	43.1	<i>n</i> -BuOH: <i>t</i> -BuNH ₂	44.8
<i>s</i> -BuNH ₂ : <i>s</i> -BuOH	35.8	<i>t</i> -BuOH: <i>t</i> -BuNH ₂	36.5

complex formation may be attributed to the fact that the contribution of the electromeric effect is more than the steric effect.

The enthalpy of complex formation between *t*-BuNH₂-*n*-BuOH (−44.8 kJ/mol) is about 1.7 kJ/mol more than that between *t*-BuOH-*n*-BuNH₂ (−43.1 kJ/mol). The probable reason for this may be found in the light of the model for amine-alcohol complex suggested by Huyskens *et al* (1960, 1963). The structures of *t*-BuNH₂-*n*-BuOH and *t*-BuOH-*n*-BuNH₂ complex are shown below (scheme 1).



In *t*-BuNH₂-*n*-BuOH complex (scheme 1) the steric repulsion between the CH₃ groups and H atoms of NH₂ group may decrease the distance between the H and oxygen atom of alcohol and favour the H bond formation. On the other hand the CH₃ group of *t*-BuOH may repel the H atoms of NH₂ away from the oxygen and weaken the H bond formation (scheme 1). So the complex formation between *t*-BuNH₂-*n*-BuOH is expected to be stronger than that between *t*-BuOH-*n*-BuNH₂.

When two tertiary molecules interact, the steric effect dominates over the isomeric effect and weakens the strength of interaction which explains the low enthalpy of self-association of tertiary butyl amine or butanol. It may be noted that the enthalpy of complex formation between the tertiary alcohol and amine (−36.5 kJ/mol) is much lower than that between the normal amine and alcohol (−42.7 kJ/mol).

In both the series; *n*-butanol-amines and *n*-butyl amine-butanols, the enthalpy of complex formation between the normal and secondary isomers is the least amongst the four isomers. In secondary butyl molecule the methyl group at α -carbon atom does not seem to make any significant electromeric contribution, probably due to the sharing of the effect between −CH₂− and functional groups. Thus the decrease in the enthalpy of complex formation may be due to the steric effect. According to this analogy it is expected that the enthalpy of complex formation between the two secondary isomers would be still smaller. It may be seen that the enthalpy of complex formation between secondary amine and alcohol (−35.8 kJ/mole) is smaller than that between the secondary and normal molecules (−40.7 kJ/mol).

4. Conclusions

From the present study the following conclusions may be drawn: Compared to the interactions between two normal isomers (i) The interactions between normal and iso-

isomers are weakened due to the steric effect of methyl group at β -carbon atom. (ii) The substitution of one methyl group at the α -carbon atom does not make significant electromeric contribution to the functional group. On the other hand due to the proximity of the CH_3 group the steric effect is more than that in the iso-isomer. (iii) In tertiary butyl molecule due to three methyl groups at the α carbon atom there is a $+I$ electromeric effect which strengthens the hydrogen bond formation. (iv) When two tertiary molecules interact, the steric hindrance outweighs the electromeric effect and the hydrogen bond becomes weaker. On the other hand when a tertiary molecule interacts with a normal isomer the steric effect is much reduced and the hydrogen bond formation is stronger due to $+I$ effect.

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