

Thermodynamic study of binary mixtures of isomeric butylamines with n-hexane: Enthalpy of hydrogen bonding*

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Abstract. Heats of mixing of normal, iso, secondary and tertiary butylamines with n-hexane have been determined at 25°C by means of a twin type calorimeter. All the four systems show an endothermic behaviour throughout the concentration range suggesting significant self association of the four isomeric butylamines. The enthalpy of the hydrogen bonding in butylamines have been found to be 8.4 kJ/mole, 7.5 kJ/mole, 6.6 kJ/mole and 4.9 kJ/mole for n-, iso-, sec- and tert-butylamines respectively. The above order of the energy of self-association has been attributed to steric hindrance to hydrogen bonding as a result of the branching of the alkyl chain.

Keywords. Heats of mixing; hydrogen bonding; thermodynamics; binary systems; butylamines-hexane.

1. Introduction

Primary and secondary amines undergo self-association due to hydrogen bond formation in their pure liquid state as well as their solutions in non-polar solvents. The mixing of n-butylamine with n-hexane (Murakami and Fujishiro 1966) is accompanied by an absorption of heat. This is attributed to the breaking of the amine-amine bonds in the self-associated n-butylamine as a result of the dilution of the amine with n-hexane. Although a number of studies (Winterhalter and Van Ness 1965a, b; Van Ness *et al* 1967; Elbe 1934; Otin *et al* 1974; Stokes and Adamson 1976) have been carried out on the determination of the enthalpy of hydrogen bonding of alcohols by studies on the heats of mixing of alcohols with non-polar solvents, little attention appears to have been paid to such studies on the amines. In this communication, we report the results of our studies on the heats of mixing of n-, iso-, sec-, and tert-butylamines with n-hexane.

2. Materials and methods

n-butylamine, a product of Riedel, sec-butylamine and iso-butylamine of Fluka, Switzerland, tert-butylamine of Merck, Germany and n-hexane of Hanawa certified as reagent grade pure chemicals were used in this work. The amines were refluxed over sodium hydroxide pellets for six hr and thereafter fractionally distilled using one

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metre long column packed with glass helices with a reflux ratio of 1 : 30. The constant boiling middle fractions were again fractionally distilled in the same manner. *n*-hexane was also purified in the same manner. Every compound was redistilled over sodium and kept over molecular sieve type 4A before use.

The heats of mixing were determined by means of a twin-type of calorimeter, similar to that described by McGlashan and others, the details of which are given elsewhere (Choudhury and Mathur 1976). In order to increase the sensitivity of the calorimetric system a 10 mV Beckmann potentiometric recorder was used, instead of 25 mV Honeywell recorder as described previously (Choudhury and Mathur 1976). All the experiments were carried out at 25°C.

3. Results and discussion

The heats of mixing of normal, iso, secondary and tertiary butylamines with *n*-hexane at 25°C over the entire concentration range are given in table 1. The data have been

Table 1. Heats of mixing of isomeric butylamine—*n*-hexane systems at 25°C

Sl. No.	x_1 Mole fraction of amine	ΔH J/mole	$\Delta H/x_1x_2$ kJ/mole
n-butylamine			
1.	0.0596	394.0	7.029
2.	0.0901	528.2	6.405
3.	0.1176	583.4	5.622
4.	0.1508	669.6	5.229
5.	0.2035	738.4	4.556
6.	0.3014	920.8	4.373
7.	0.4531	1012.4	4.086
8.	0.6262	889.9	3.802
9.	0.8000	599.0	3.744
iso-butylamine			
1.	0.0619	375.4	6.466
2.	0.1000	514.7	5.719
3.	0.1513	714.4	5.565
4.	0.2354	827.3	4.350
5.	0.3598	867.9	3.816
6.	0.5023	841.2	3.364
7.	0.6693	691.3	3.123
8.	0.7987	434.3	2.701
sec-butylamine			
1.	0.0617	341.9	5.903
2.	0.1060	541.8	5.717
3.	0.1517	668.1	5.189
4.	0.1993	780.9	4.894
5.	0.3502	863.1	3.793
6.	0.5057	815.0	3.260
7.	0.7031	577.8	2.768
8.	0.7965	423.2	2.611
9.	0.8899	224.5	2.290
tert-butylamine			
1.	0.0603	252.3	4.453
2.	0.1117	449.7	4.532
3.	0.1994	697.9	4.405
4.	0.2742	826.0	4.151
5.	0.3654	914.7	3.945
6.	0.4950	913.0	3.652
7.	0.7000	673.9	3.209
8.	0.8537	379.9	3.042

fitted in a series equation of the type $\Delta H(\text{J/mole}) = Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5 + Fx^6$ using a Honeywell-400 computer; where A, B, C, D, E and F are constants and x is the mole fraction of the butylamine. The values of the constants for all the four systems are reported in table 2. The variation of the heats of mixing (ΔH) as a function of the mole fraction of butylamine (x_1) for the four binary systems studied by us is shown in figure 1 for easy comparison.

All the four isomeric butylamines have an endothermic heats of mixing with n -hexane. The high endothermic heats of mixing observed in the present work may be attributed to the breaking of the amine-amine bonds in the self-associated butyl-

Table 2. The least square constants of the equation $\Delta H = Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5 + Fx^6$ for the heats of mixing of the isomers of butylamine with n -hexane at 25°C

System	A $\times 10^8$	B $\times 10^4$	C $\times 10^9$	D $\times 10^4$	E $\times 10^4$	F $\times 10^4$
<i>n</i> -butylamine	9.30528	-5.45916	194.387	-36.1749	32.0476	-10.7810
iso-butylamine	7.00087	-1.71807	1.88511	5.32614	-7.88837	3.39173
sec-butylamine	6.49064	-1.43147	1.29518	3.37099	-4.51731	1.79938
tert-butylamine	4.45333	-0.28157	-15.8582	3.37100	-2.81489	0.86601

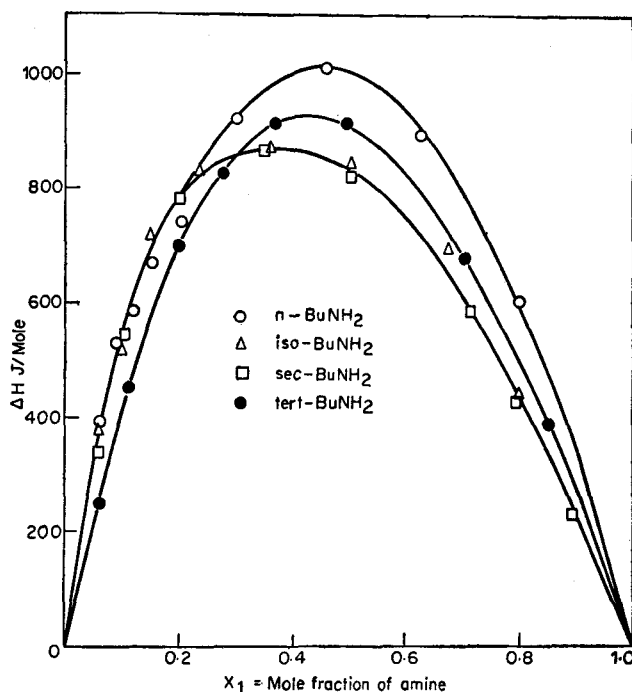


Figure 1. ΔH vs X_1 plots for isomers of butylamine (1)- n -hexane (2) systems at 25°C.

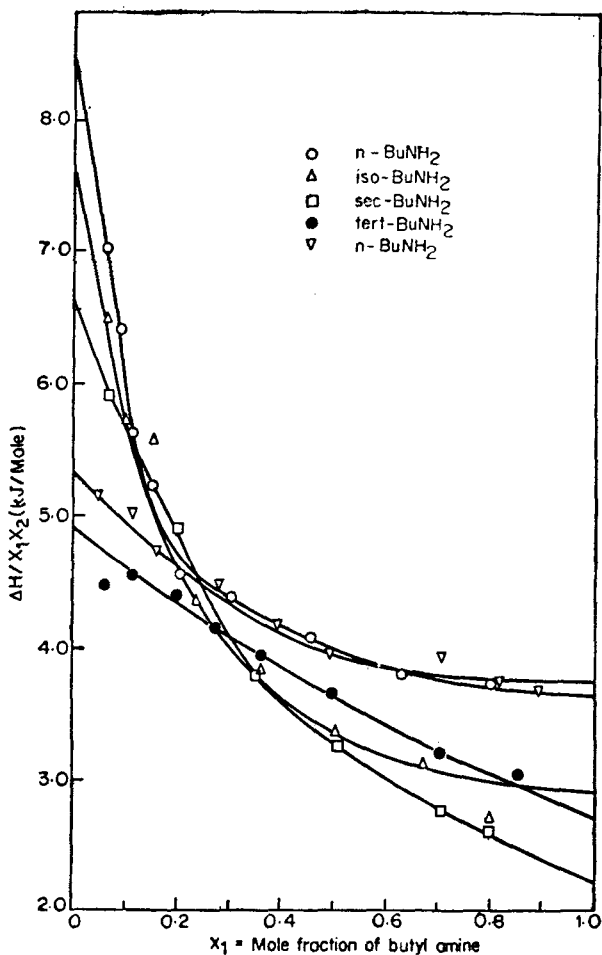


Figure 2. $\Delta H/X_1 X_2$ vs plots for isomeric butylamine (1)-*n*-hexane systems at 25°C. ∇ *n*-BuNH₂ (Murakami and Fujishiro, 1966).

amine molecules. The heats of mixing of sec-butylamine and iso-butylamine with *n*-hexane are almost identical. All the experimental values of the heats of mixing for both the amines fall on a single smooth ΔH vs x_1 plot and the maximum heat of mixing is the same i.e. 865 J/mole at the same mole fraction of butylamine i.e. 0.360. Similarly the plots of ΔH versus x_1 for *n*-butylamine and tert-butylamine are also similar in nature. The maximum heat of mixing is also found at nearly the same mole fraction of butylamine viz. 0.455 mole fraction. The symmetry of ΔH versus x_1 curves in figure 1 shows that the butylamine isomers form two groups: one of normal and tertiary butylamines and the other of iso- and secondary butylamines.

Schug and Chang (1971) studied the PMR spectra of these butylamine isomers at different concentrations in cyclohexane and concluded that the best self-association model for all the four isomers is the formation of a non-cyclic trimer. They calculated the association constants in terms of mole-fraction units as, 2.30, 2.75, 3.95 and

4.25 for tert-, normal-, sec- and iso-butylamines respectively. It may be noted that the association constants of tert-BuNH₂ and n-BuNH₂ are close to each other (2.50 ± 0.25). The sec-BuNH₂ and iso-BuNH₂ have also association constants close to each other (4.10 ± 0.15) but significantly higher than those of t- and n-butylamines. The results of Schug and Chang (1971) on the association constants and our results on the heats of mixing suggest a broad classification of the four isomeric butylamines into two groups.

The $\Delta H/x_1x_2$ versus x_1 plots, where x_1 is the mole fraction of butylamine are represented in figure 2. The curves have been extrapolated to zero concentration of butylamine in n-hexane. The values of the heats of mixing when extrapolated to infinite dilution in n-hexane represent the partial molar enthalpies of mixing of butylamines and are a measure of the hydrogen bond energies of self-association of these four isomeric amines (Choudhury and Mathur 1976).

The enthalpy of self-association of n-butylamine at 25°C has been found to be 8.4 kJ/mole in the present work while Murakami and Fujishiro (1966) had earlier reported the value of 5.3 kJ/mole for the same system by the same method. The experimental data of the Japanese workers of the above reference are also shown in figure 2 for ready comparison.

Lambert and Strong (1950) calculated the energy of dimerisation of ethyl and methyl amines from the second virial coefficient measurements. The energy of dimerisation was found to be 3.6 and 3.4 kcal per mole for ethylamine and methyl amine respectively. Pimentel and McClellan (1960) have suggested that the NH...N bond energy in the case of amines is of the order of 3 to 5 kcal/mole. Wolf and Wurtz (1970) calculated the energy of self-association of isotopic dimethyl amines from vapour pressure data found to be 1.82 kcal/mole. Wolf and Garner (1972) determined the energy of self-association of dimethyl amine in n-hexane by infrared spectroscopy and the energy was found to be 1.85 kcal/mole. Lady and Whetsel (1964) found that ΔH for self-association of aniline as 7.7 ± 0.5 kcal/mole of the tetramer. The histograms given by Murthy and Rao (1968) suggest that the hydrogen bond energy of self-association of amines lies in the range of 2 to 5 kcal/mole. All these studies indicate that the energy of NH...N bond is of the order of 2.0 kcal per

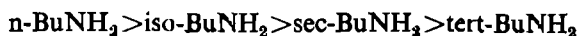
Table 3. Enthalpies of hydrogen bonding and heats of vapourisation of butylamine isomers at 25°C

Isomer	Enthalpy of hydrogen bonding ΔH^H kJ/mole	Heat of vapourisation* ΔH^V kJ/mole	Change with respect to n-butylamine	
			ΔH^H kJ/mole	ΔH^V kJ/mole
n-butylamine	8.4	34.98	—	—
iso-butylamine	7.5	33.47	0.90	1.50
sec-butylamine	6.6	32.61	1.80	2.36
tert-butylamine	4.9	29.68	3.60	5.29

*(Riddick and Bunger 1970)

mole. It appears therefore that the hydrogen bond energy of 5.3 kJ/mole (1.27 kcal/mole) for self-association of n-butylamine obtained by Murakami and Fujishiro (1966) is rather low. The value of 8.4 kJ or 2.03 kcal/mole obtained in the present work appears to be in agreement with the expected value of hydrogen bonding of NH...N bond.

The enthalpies of hydrogen bonding on self-association of the four isomeric butylamines as well as their heats of vapourisation at 25°C are given in the table 3. It will be observed that both the enthalpy of hydrogen bonding and the heats of vapourisation at 25°C, follow the order:



The ratios of the decrease in the enthalpies of hydrogen bonding and the heats of vapourisation with respect to n-butylamine, also given in table 3 for iso-, sec-, and t-butylamines are similar as the branching of the alkyl chain increases from iso- through secondary to tertiary BuNH₂.

The decrease in the hydrogen bond energy of self-association of butylamine on branching of the alkyl chain may be related to the position of the substituent methyl group in the alkyl chain of the amine. The observed reduction in the hydrogen bond energy may be attributed to the net contribution of two mutually oppressing forces: (i) The electrometric effect (or the + I effect) which increases the electron density at the nitrogen atom resulting in an increase in the energy of the hydrogen bond, (ii) The steric effect which will hinder the self-association and hence decreases the energy of association.

It is expected that among the isomeric butylamines, the tert butylamine would have maximum steric effect as two methyl group are substituted at the alpha carbon atom, followed by sec-butylamine where one methyl group is substituted at the alpha carbon atom. The iso-butylamine will have the smallest steric effect as the methyl group is substituted at the beta-carbon atom. From the steric effect point of view only the enthalpy of self-association of these butylamine isomers is expected to decrease in the order:



The fact that the observed order of enthalpy of hydrogen bonding is in accordance with the above order alone indicates that the contribution of +I effect is small in comparison to the steric effect.

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