

Thermodynamic study of binary mixtures of isomeric butylamines with methanol enthalpy of hydrogen bonded complex*

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Abstract. Heats of mixing of the binary mixtures of *n*-, *sec*-, *iso*- and *t*-butylamines with methanol were determined in the entire concentration range. All the four systems showed a strong exothermic behaviour. The exothermic heats of mixing vary in the order $t\text{-BuNH}_2 > n\text{-BuNH}_2 > sec\text{-BuNH}_2 > iso\text{-BuNH}_2$. The enthalpy of hydrogen bond in the methanol-butylamine complexes was calculated by means of a thermochemical cycle and found to vary in the order $t\text{-BuNH}_2 > n\text{-BuNH}_2 > iso\text{-BuNH}_2 > sec\text{-BuNH}_2$. This order is different than that found for the hydrogen bond due to self-association. The difference has been explained in the light of steric and electromeric effects arising out of the substitution of the methyl groups in the alkyl chain of the butylamine.

Keywords. Heats of mixing; butylamine-methanol; thermodynamics; binary systems; enthalpy of complexes.

1. Introduction

The existence of both intra- and inter-molecular hydrogen bonds has been recognised for quite some time. The primary and secondary amines and the alcohols have both a proton donor and a proton acceptor group. It is expected that there would be a significant hydrogen bonding on account of the self-association in the pure state of such compounds and in addition, the mutual association in their binary mixtures. In a previous paper, the hydrogen bond energy associated with the self-association of the four isomeric butyl amines has been determined from the results on the heats of mixing of the butylamines with *n*-hexane (Pradhan and Mathur 1978). In the present paper our results on the heats of mixing of methanol with *n*-, *iso*-, *sec*- and *tert*-butylamines and on the variation of the hydrogen bond energy with the increase in the branching of the alkyl chain of the butylamine are presented.

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2. Materials and methods

The purification method for four isomeric butylamines has been described earlier (Pradhan and Mathur 1978). Guaranteed grade methanol obtained from M/s. Sarabhai Merck, was refluxed on alkaline silver nitrate and then fractionally distilled over a metre long column packed with glass helices. The purity of the constant boiling middle fraction was confirmed by gas liquid chromatography (GLC) and density measurement. The methanol was dried by passing through a column of freshly activated type 4A molecular sieves before use in the experiments on the heats of mixing which were determined by a twin type of calorimeter. The details of the calorimeter were described in earlier communication (Pradhan and Mathur 1978).

3. Results and discussion

The heats of mixing of normal butylamine with methanol were determined at 25° C over the entire concentration range. The results are given in table 1. The heats of mixing of the binary mixtures of iso-, sec- and tert-butylamines with methanol were determined at 25° C for the entire concentration range. In order to find out the excess heat capacity of these systems, the heats of mixing were also determined at 40° C at selected few concentrations in the region of maximum heats of mixing. Our results on iso-, sec-, and tert-butylamines at 25° C and 40° C are given in tables 2 to 4 respectively.

Table 1. Heats of mixing of methanol (1)-*n* butylamine (2) system at 25° C.

x_1 Mole fraction of methanol	ΔH J/mole	$\Delta H/x_1x_2$ KJ/mole
0.1506	-1586.7	-12.404
0.2180	-2132.4	-12.509
0.2915	-2782.4	-13.472
0.3555	-3185.8	-13.905
0.4469	-3717.6	-15.040
0.5433	-3901.0	-15.722
0.6337	-3758.0	-16.150
0.7250	-3390.8	-17.007
0.7785	-2915.8	-16.909
0.8140	-2556.3	-16.884
0.8340	-2093.2	-15.304
0.8627	-1981.0	-16.724
0.8938	-1393.6	-15.191
0.9259	-909.7	-13.180

Table 2. Heats of mixing of methanol (1)-iso-butylamine (2) at 25° C and 40° C.

x_1 Mole fraction of methanol	ΔH J/mole	$\Delta H/x_1x_2$ KJ/mole
25° C		
0.0418	- 344.5	- 8.601
0.0857	- 749.9	- 9.571
0.1522	-1392.0	-11.407
0.1982	-1856.2	-11.680
0.2583	-2419.7	-12.630
0.3033	-2813.1	-13.313
0.3971	-3267.3	-13.647
0.4775	-3502.6	-14.039
0.5780	-3541.0	-14.517
0.6584	-3304.0	-14.690
0.7670	-2727.4	-15.262
0.8206	-2266.5	-15.396
0.8983	-1397.5	-15.297
40° C		
0.4010	-3170.5	
0.4913	-3265.2	
0.5986	-3339.5	
0.6914	-2939.9	

Table 3. Heats of mixing of methanol (1)-sec-butylamine (2) at 25° C and 40° C

x_1 Mole fraction of methanol	ΔH J/mole	$\Delta H/x_1x_2$ KJ/mole
25° C		
0.0571	- 484.5	- 8.999
0.1146	-1058.6	-10.433
0.1983	-1904.5	-11.980
0.2613	-2423.3	-12.555
0.3326	-2902.6	-13.016
0.4017	-3328.1	-13.848
0.4608	-3468.0	-13.958
0.5717	-3580.2	-14.622
0.6791	-3353.8	-15.390
0.7344	-2948.8	-15.118
0.8018	-2310.8	-14.541
0.8714	-1860.6	-16.603
0.9390	- 962.7	-16.807
40° C		
0.3952	-3110.8	
0.4911	-3415.2	
0.5989	-3353.2	
0.6821	-3063.8	

Table 4. Heats of mixing of methanol (1)-tert-butylamine(2) at 25° C and 40° C.

x_1 Mole fraction of methanol	ΔH J/mole	$\Delta H/x_1x_2$ KJ/mole
25° C		
0.0378	- 307.6	- 8.458
0.0528	- 721.9	-14.435
0.0958	-1165.6	-13.502
0.1016	-1234.0	-13.519
0.1069	-1314.7	-13.771
0.1466	-1764.4	-13.998
0.1982	-2392.9	-15.058
0.2600	-2952.9	-15.348
0.2642	-3142.4	-16.165
0.3128	-3507.5	-16.318
0.3909	-4165.7	-17.496
0.4948	-4672.7	-18.693
0.5973	-4776.1	-19.856
0.6045	-4537.4	-18.979
0.7244	-3923.2	-19.651
0.7913	-3303.0	-20.001
0.8742	-2263.0	-20.576
0.8784	-2012.4	-18.841
0.9522	- 687.0	-15.114
40° C		
0.4041	-3848.1	
0.5150	-4321.6	
0.5989	-4342.8	
0.7409	-3438.0	

The data obtained at 25° C for these systems have been fitted in a series equation of the type ΔH (KJ/mole) = $Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5 + Fx^6$, by using a Honeywell-400 computer, where A, B, C, D, E and F are the constants and x is the mole fraction of methanol. The values of the constants are given in table 5.

The variation of heats of mixing at 25° C as a function of methanol concentration (x) is presented in figure 1. It will be observed that all the four systems showed highly exothermic behaviour. The ΔH versus x_1 curves have the shape of a nearly symmetrical parabola. The maximum heats of mixing are obtained at nearly 0.5 mole fraction of the methanol. Our results on the heats of mixing of *n*-butylamine-methanol systems are in very good agreement with the previously reported data (Duttachoudhury and Mathur 1976; Nakanishi *et al* 1970).

The variation of the heats of mixing of methanol with both *sec*-butylamine and *iso*-butylamine as a function of the mole fraction of the alcohol can be described by a single smooth curve of ΔH versus x_1 . This behaviour is similar to that observed in the case of secondary and *iso*-butylamines with *n*-hexane systems (Pradhan and Mathur 1978).

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

System	$A \times 10^3$	$B \times 10^4$	$C \times 10^4$	$D \times 10^6$	$E \times 10^4$	$F \times 10^4$	STD error J/mole
<i>n</i> -butylamine	-11.01664	0.079862	3.107072	-0.812245	10.96829	-4.928875	65.2
Iso-butylamine	-7.094053	-2.64485	9.277683	-1.070306	6.06036	-1.279774	48.1
Sec-butylamine	-7.538867	-2.328013	8.724202	-1.087778	7.05115	-1.81819	76.0
Tert-butylamine	-10.58017	-2.385511	11.58559	-2.059716	19.71754	-7.260186	92.0

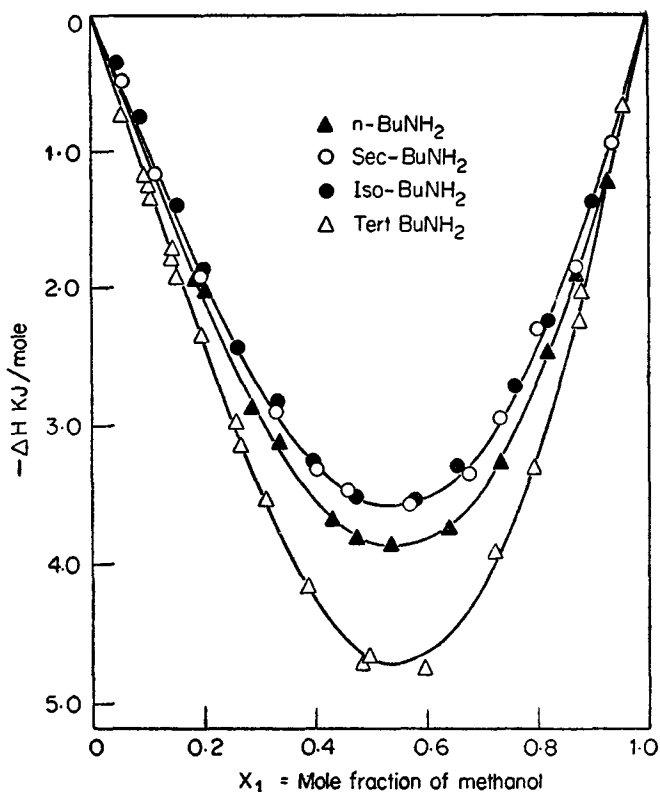
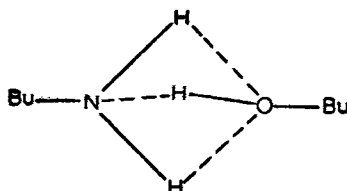


Figure 1. ΔH vs x_1 plot for methanol (1)—isomer of butylamine (2) systems at 25° C.

The enthalpies of mixing of iso-butylamine, sec-butylamine and tertiary-butylamine with methanol at 40° C in the region of 0.5 mole fraction of methanol were found to be about 6%, 5% and 7% respectively lower than those obtained at 25° C indicating that the excess heat capacity $C_p^E = d(\Delta H)/dt$ is a positive quantity for each of the above alcohol-amine systems. A similar behaviour was also reported by Duttachoudhury and Mathur (1976) for *n*-butylamine-methanol system. According to Goates *et al* (1959) and Mckinnon and Williamson (1964) a positive excess heat capacity for a binary mixture indicates the existence of specific attractive interactions between the solute and solvent molecules. Studies on the binary mixtures of *n*-butylamine with different aliphatic alcohols by Duttachoudhury and Mathur (1976), Murakami and Fujishiro (1966), Huyskens and co-workers (Huyskens and Huyskens 1960; Lambert and Huyskens 1963) indicate that *n*-butylamine forms a hydrogen bonded complex molecule with an aliphatic alcohol. The high exothermic heats of mixing described in the present study can therefore be attributed to the formation of hydrogen bonded amine-alcohol complex.

The exact mode of self-association of methanol is still debatable (Ventil *et al* 1957; Tucker *et al* 1969; Saunders and Hyne 1958; Dixon 1970; Murthy 1970; Fletcher and Meller 1968; Van Ness *et al* 1967). Murthy (1970) on the basis of IR spectroscopic study concluded that the methanol essentially exists as monomers and dimers while other workers (Saunders and Hyne 1958; Dixon 1970) suggest

a monomer-tetramer model. Similarly aliphatic amines are also known to exist in different polymeric species (Schug and Chang 1971; Lambert and Strong 1950; Feeney and Sutcliffe 1961; Wolff *et al* 1964). It is therefore difficult to predict the nature of the specific interaction between methanol and isomeric butylamines. Huyskens and Huyskens (1960) and Lambert and Huyskens (1963) have studied the *n*-butylamine-*n*-butanol system by NMR, calorimetry and conductivity. They concluded from their studies that the *n*-butylamine and *n*-butanol form a non-linear complex and suggested its structure (structure 1).



In our previous work on the volume change on mixing it has been observed that all the four binary systems exhibit a negative volume change on mixing. The plots of volume change on mixing as a function of mole fraction of methanol are symmetrical and the maxima are at nearly 0.5 mol fraction (Pradhan 1979). It is therefore reasonable to assume that the methanol-butylamine complex is essentially 1 : 1 type; although the presence of a certain amount of A_iB_j type of species cannot be ruled out.

In spite of the difficulty in formulating a specific model for the structure of binary mixtures of methanol with the isomeric butylamines, the problem of methanol-butylamine interaction can be approached from a purely thermodynamic standpoint. The pronounced exothermic effect accompanying the mixture of methanol with any one of the isomeric butylamines may be attributed to a net effect of the following three heat effects:

- (i) Endothermic effect: $\Sigma n_i \Delta H_i$ due to the breaking of alcohol-alcohol bonds on dilution with butylamine. The n_i is the number of $-\text{OH} \cdots \text{OH}$ bonds broken and ΔH_i is the heat associated with the breaking of each such bond.
- (ii) Endothermic effect: $\Sigma n_j \Delta H_j$ due to the breaking of amine-amine bonds of associated amine molecules by dilution with methanol where n_j is the number of amine-amine bonds broken and ΔH_j is the heat associated with the breaking of each such bond.
- (iii) Exothermic effect: $\Sigma n_{ij} \Delta H_{ij}$ associated with the formation of alcohol-amine bonds where n_{ij} is the number of such bond and H_{ij} is the enthalpy of formation of each bond in A_iB_j complexes.

The contribution of the non-specific interactions to the total heat change may be neglected as it is small compared to the large heat changes associated with the breaking and the forming of the hydrogen bonds. Hence the enthalpy of mixing is given as:

$$\Delta H = \Sigma n_i \Delta H_i + \Sigma n_j \Delta H_j - \Sigma n_{ij} \Delta H_{ij} \quad (1)$$

The hydrogen bond energy of the methanol-butylamine complex (ΔH_{ij}) is determined by using a thermochemical cycle (see figure 2).

3.1 Thermochemical cycle

The system contains 1 mol of methanol (A), x moles of amine (B) and y moles of n -hexane (H), such that

$$y \gg x \gg 1.$$

The total heat change in going from state I to state IV (see figure 2) is calculated by considering the following five processes :

Process—1 : 1 mol of methanol (A) diluted to infinite dilution in n -hexane.

Process—2 : x mol of amine (B) diluted to infinite dilution in n -hexane.

Process—3 : Mixing of 1 mol of methanol with x mol of amine resulting in the formation of 1 mol of AB complex at infinite dilution in excess of amine.

Process—4 : State—III is transferred to state—IV by diluting with a large quantity of n -hexane without breaking the AB complex.

Process—5 : Mixing of 1 mol of alcohol (A) at infinite dilution in n -hexane with x mol of amine (B) at infinite dilution to give a hypothetical state—IV in which 1 mol of AB complex and $(x-1)$ mol of amine both are present at infinite dilution in n -hexane.

The enthalpy of A - B complex formation equals the enthalpy change ΔH_5 from state—II to state—IV. This enthalpy change can be calculated from the thermochemical cycle, viz.

$$\Delta H_1 + x\Delta H_2 + \Delta H_5 = \Delta H_3 + \Delta H_4$$

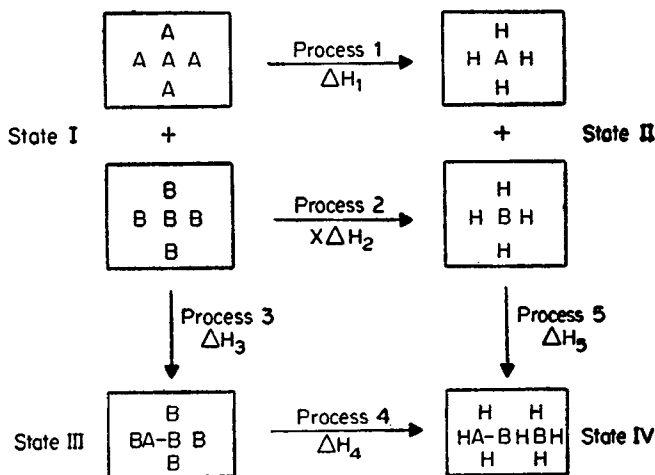


Figure 2. Thermochemical cycle.

$$\text{or } \Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + \Delta H_4 \quad (2)$$

where ΔH_1 and ΔH_2 are respectively the partial molar enthalpy of mixing of methanol and amine at infinite dilution in *n*-hexane. The ΔH_3 is the partial molar enthalpy of mixing of methanol at infinite dilution in butylamine. Two separate terms contribute to ΔH_4 , viz.

- (i) ΔH_4^{BH} , the enthalpy of dilution of $(x - 1)$ mol of butylamine by a large excess of *n*-hexane which is equal to $(x - 1)H_2$.
- (ii) ΔH_4^d , the difference in the dipolar stabilisation enthalpy of *AB* complex dipole arising from the reaction field of butylamine and *n*-hexane media. The eqn. (2) can then be written as:

$$\Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + (x - 1)\Delta H_2 + H_4^d,$$

$$\text{or } \Delta H_5 = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d. \quad (3)$$

The value of ΔH_1 is obtained by extrapolating the curve of $\Delta H/x_1x_2$ versus x_1 , where x_1 is the mole fraction of methanol, to infinite dilution of methanol ($x_1 \rightarrow 0$). The data for this were used from the literature (Van Ness *et al* 1967; Pahlke *et al* 1935). The values of ΔH_2 were taken in a similar manner from our previous work (Pradhan and Mathur 1978). The values of ΔH_3 were obtained by extrapolating the $\Delta H/x_1x_2$ versus x_1 , where x_1 is the mole fraction of methanol to zero concentration of methanol in amine. The plots of $\Delta H/x_1x_2$ as a function of mole fraction of methanol (x_1) are given in figure 3.

The dipolar stabilisation energy ΔH^d of the complex is the difference of two terms which may be represented as

$$\Delta H^d = \Delta H^d - \Delta H_B^d \quad (4)$$

where ΔH^d is the dipolar stabilisation energy of the complex in *n*-hexane medium and ΔH_B^d is that in the amine medium.

The dipolar stabilisation enthalpy of a dipole in a medium *i* can be calculated from the expression

$$\Delta H_i = d(\Delta G_i/T)/d(1/T) \quad (5)$$

where ΔG_i is the dipolar stabilisation free energy of dipole in medium *i* which is calculated by the equation (Buttcher 1952)

$$G_i = -1/2 f \cdot \mu^2 (1 - a \cdot f). \quad (6)$$

The values of *f* are given by the expression

$$f = 2(\epsilon - 1)/a^3(2\epsilon + 1) \quad (7)$$

where ϵ is the dielectric constant of the medium, *a* is the molecular radius and *a* is the molecular polarisability. The molecular radius and polarisability are given by the expressions

$$a = (3M/4\pi Nd), \quad (8)$$

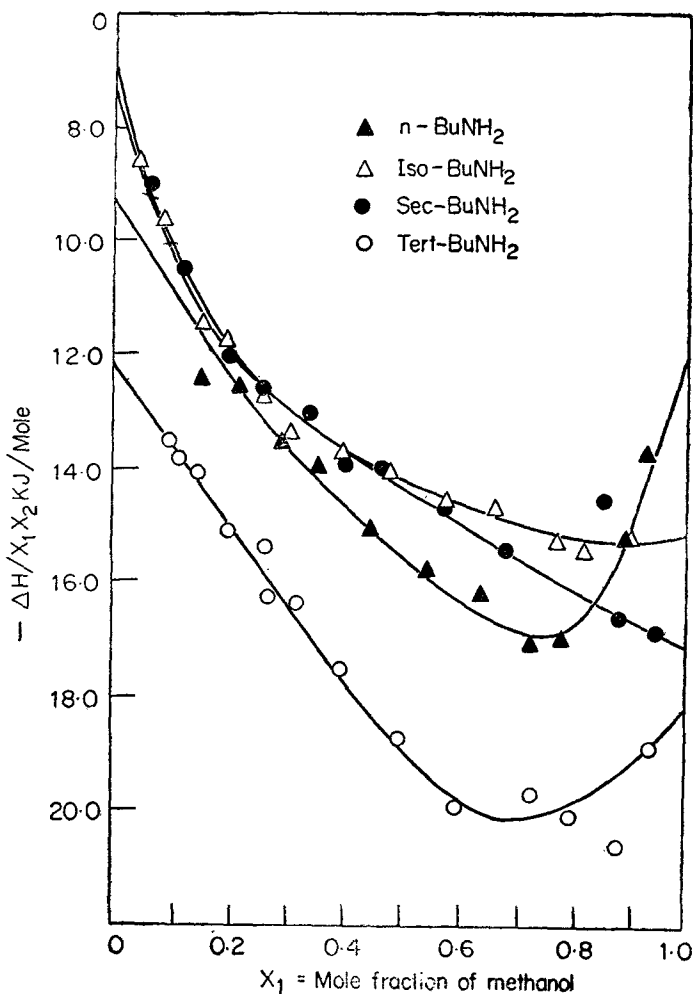


Figure 3. $\Delta H/x_1x_2$ vs x_1 curves for methanol (1)—butyl amine isomer (2) systems at 25° C.

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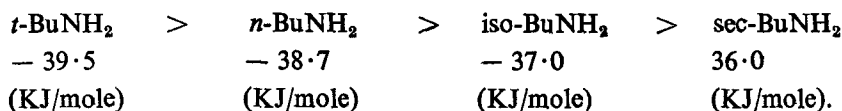
$$a = a^3 [(n^2 - 1)/(n^2 + 1)], \quad (9)$$

where M , n , d and N are the molecular weight, internal refractive index, density of the compound and the Avogadro's number respectively.

Clerbaux *et al* (1967) reported the dipole moment of *n*-butylamine-*i*-butanol complex to be 2.31×10^{-18} e.s.u. The dipole moments of methanol and *n*-butanol are very close (Smyth 1955), i.e., 1.66D and 1.69D respectively. Similarly the dipole moments of the four amines, viz. *n*-, iso, sec, and tert, butylamines are also sufficiently close, i.e., 1.37D, 1.27D, 1.28D and 1.29D respectively. It has therefore been assumed that the dipole moment of 1 : 1 methanol complex with different isomers of butylamine is the same as that of *n*-butylamine-*i*-butanol complex, i.e., 2.31D.

The data necessary for the calculations of ΔG_f and hence ΔH_H^g and ΔH_B^g are summarised in table 6. The molecular radii and the polarisabilities of the amine-methanol complexes have been assumed to be equal to the sum of the corresponding values of the component molecules. The values of ΔH_1 , ΔH_2 , ΔH_3 and ΔH_4^g of eqn. (3) and the ultimate enthalpy of hydrogen bonded complex formation are reported in table 7.

The enthalpy of methanol-amine complex of the four butylamine isomers has the following order:



The branching of alkyl chain of butylamine will give rise to two mutually opposing effects:

- (i) A decrease in the strength of the $\text{N}\cdots\text{H}$ bond as a result of the steric hindrance produced by the substitution of methyl group in the alkyl chain of the butylamine.

Table 6. Values of the constants used for the calculations of the dipolar stabilisation energies of the methanol-butylamine complexes.

Compound	Temperature °C	Density	$a^3 \times 10^{23}$ cc	Refractive index (Riddick and Bunger 1970)	$\alpha (\times 10^{23})$	Dielectric constant (Riddick and Bunger 1970)
Methanol	20	0.79131	1.602	1.3287	1.3287	..
	25	0.78653	1.612	1.3269	0.3261	..
	30	0.78175	1.622	1.3251	0.3264	..
N-butylamine	20	0.7369	3.936	1.4014	1.2828	5.34
	25	0.7323	3.961	1.3987	1.2836	5.16
	30	0.7277	3.986	1.3960	1.2841	4.98
Iso-butylamine	20	0.7289	3.979	1.3972	1.2843	4.31
	25	0.7241	4.006	1.3945	1.2854	4.22
	30	0.7193	4.032	1.3918	1.2861	4.13
Sec-butylamine	20	0.7218	4.018	1.3934	1.2855	4.34
	25	0.7173	4.044	1.3907	1.2862	4.26
	30	0.7128	4.069	1.3880	1.2865	4.18
Tert-butylamine	20	0.6917	4.193	1.3788	1.2942	4.26
	25	0.6867	4.224	1.3761	1.2956	4.19
	30	0.6817	4.255	1.3734	1.2967	4.12
n-hexane	20	1.890
	25	1.883
	30	1.876

Table 7. The enthalpy of methanol-butylamine complexes calculated by eqn. (3).

System	$\Delta H_1 = \lim_{x_1 \rightarrow 0} \frac{\Delta H}{x_1 x_2}$ KJ/mole	$\Delta H_2 = \lim_{x_1 \rightarrow 0} \frac{\Delta H}{x_1 x_2}$ KJ/mole	$\Delta H_3 = \lim_{x_1 \rightarrow 0} \frac{\Delta H}{x_1 x_2}$ KJ/mole	$\Delta H_4 = \lim_{x_1 \rightarrow 0} \frac{\Delta H}{x_1 x_2}$ KJ/mole	ΔH_4^* KJ/mole	Enthalpy of complex KJ/mole
Methanol(1)- <i>n</i> -hexane(2)	24.7
<i>N</i> -butylamine(1)- <i>n</i> -hexane(2)	..	8.4
Iso-butylamine(1)- <i>n</i> -hexane	..	7.5
Sec-butylamine(1)- <i>n</i> -hexane(2)	..	6.6
Tert-butylamine(1)- <i>n</i> -hexane(2)	..	4.9
Methanol(1)- <i>n</i> -butylamine(2)	-9.2	3.6	-38.7	-38.7
Methanol(1)-iso-butylamine(2)	-7.5	2.7	-37.0	-37.0
Methanol(1)-sec-butylamine(2)	-7.2	2.5	-36.0	-36.0
Methanol(1)-tert-butylamine(2)	-12.1	2.2	-39.5	-39.5

* Calculated by equations 4 and 5.

- (ii) An increase in the strength of the hydrogen bond on account of the electro-meric effect (+ I effect) which increases the electron density at nitrogen atom of the amino group.

The steric effect is expected to be maximum in the case of *t*-butylamine where two methyl groups are substituted at alpha carbon atom. It should be followed by *sec*-butylamine and *iso*-butylamine due to substitution of one methyl group at alpha and beta carbon atoms respectively. The *n*-butylamine is expected to have no steric effect. Hence, in case the magnitude of the steric effect is much larger than the magnitude of electromeric + I effect, the strength of the hydrogen bond in methanol-butylamine complexes is expected to decrease as



In the case of self-association of the four butylamine isomers the strength of hydrogen bond does follow the above order. However, in the interaction of the four butylamine-alcohol isomeric butylamines with the methanol, although the *n*-butylamine, *iso*-butylamine, and the *sec*-butylamine complexes with methanol, follow the above order of decreasing strength of the hydrogen bond, the hydrogen bond in the *t*-butylamine-methanol complex is the strongest indicating that the magnitude of the electromeric effect in this case is greater than the steric effect. Supporting evidence to this conclusion is available from the work of Geisler *et al* (1971) on the 1 : 1 binary mixtures of *n*-butyl alcohol with *iso*-, *sec*-, and *tert*-butyl alcohol. The 1 : 1 mixture of *n*-butyl alcohol with *iso*-butyl alcohol and *sec*-butyl alcohol did not show any deviation from the ideal behaviour, but the *n*-butanol-*t*-butanol mixture showed a significant deviation from ideal behaviour indicating a strong interaction. The strong interaction between the *n*-butanol and *t*-butanol was attributed to electromeric effect on account of the substitution of the two methyl groups at the alpha carbon atom in *t*-butanol.

It, therefore, appears from the results of our studies on the mixtures of methanol with the four isomeric butyl amines that the steric effect dominates over the + I effect (Pradhan and Mathur 1978; Geisler *et al* 1971) during the self-association of *t*-butylamine, yet in the interaction between a tertiary molecule and a dissimilar molecule like normal alcohol, the + I effect dominates over the steric effect. The greater strength of the hydrogen bond methanol-*tert*-butylamine complex may therefore be attributed to the electromeric effect of the two methyl groups substituted at the alpha carbon atom of the alkyl chain in the amine.

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