Heats of Mixing of Binary Mixtures of n-Butylamine with Water, Methanol, Ethanol & n-Butan-1-ol: Effect of the Chain Length on Hydrogen Bond Energy*

M. K. DUTTA-CHOUDHURY† & H. B. MATHUR‡

National Chemical Laboratory, Poona 411008

The heats of mixing for the binary mixture of n-butylamine with water, methanol, ethanol and 1-butanol have been measured at 25°. These results along with those available in literature have been used to calculate the values of thermodynamic excess functions G^E, H^E, TS^E. The positive values of $\frac{\partial H^E}{\partial T} = C_P^E$ and the nagative values of H^E, G^E, TS^E and V^E for these systems indicate strong specific interaction of n-butylamine with the n-alcohols and water. The nearly symmetrical parabolic plots of H^E, G^E, TS^E and V^E as a function of the mole fraction of alcohol and the presence of the maxima in those curves close to 0·5 mole fraction of alcohol suggest a predominant 1:1 alcohol-amine interaction. The energies of the hydrogen bond between n-butylamine and (C_1-C_4) n-alcohols have been determined from a thermochemical cycle. It has been observed that the hydrogen bond energy between n-butylamine and (C_2-C_4) n-alcohols has a constant value of $35\cdot5 \pm 2$ kJ mole⁻¹ with the exception of the n-butylamine+methanol hydrogen bond which has a slightly higher energy of $37\cdot5 \pm 2$ kJ mole⁻¹.

IN an earlier communication[1] we made use of a thermochemical cycle to determine the hydrogen bond energy associated with the interaction of n-butylamine with 1-propanol from the results of the heats of mixing. It is now fairly well established that the energy of a hydrogen bond may be considered to be the sum of four terms[2], viz. (i) electrostatic energy, (ii) dispersive energy, (iii) exchange repulsion, and (iv) delocalization energy due to electron transfer from a proton acceptor to a proton donor. One cannot, however, easily estimate the contribution of each of these forces to the overall energy of the hydrogen bond either experimentally or by exact theoretical calculations. It is, therefore, useful to investigate how the energy of the hydrogen bond varies with the nature of a proton donor and/or a proton acceptor. We report in this paper, the results of our studies on the heats of mixing for the binary mixtures of n-butylamine with water, methanol, ethanol and n-butan-1-ol and on variation, if any, of the hydrogen bond energy with an increase in the chain length of the alcohols.

Materials and Methods

The heats of mixing of the binary mixtures of n-butylamine with water, methanol, ethanol and 1-butanol at 25° ± 0·1° have been measured with a twin calorimeter system described earlier[3]. The methods of purification of the chemicals and checking of their purity have also been described in an earlier communication[3].

Results and Discussion

The heats of mixing of n-butylamine with water, methanol, ethanol and 1-butanol at 25° are given in Table 1, where x_1 is the mole fraction of water or alcohol and H^E (or ΔH^m) is the heat of mixing expressed in kJ mole⁻¹ of the mixture. The results of the heats of mixing have been fitted by the method of least squares to a three constant Redlich-Kister equation of the type

$$H^E(\text{kJ/mole}) = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2] \quad \ldots (1)$$

where x_1 and x_2 are the mole fractions of water/alcohol and n-butylamine respectively. The values of the constants of Eq. (1) for all these systems and also for 1-propanol + n-butylamine system reported earlier[1,3], at 25° and 40° (ref. 3) are given in Table 2. The mixing of water with n-butylamine is an exothermic reaction throughout the entire range of concentration. The plots of H^E versus x_1 have the shape of a parabola with the value of H^E at maxima at 25 and 40° equal to $-3\cdot48$ and $-3\cdot36$ kJ mole⁻¹ at water mole fraction of 0·522 and 0·547 respectively. An increase of temperature from 25° to 40° brings about a small decrease in the magnitude of the exothermic heats of mixing.

The values of H^E as a function of x_1 for the binary mixtures of n-butylamine with methanol, ethanol and 1-butanol like the n-butylamine+water and n-butylamine+1-propanol[1] mixtures, lie on nearly symmetrical parabolic curves with maxima close to 0·5 mole fraction of the alcohols as shown in Table 2 which also shows that an increase in temperature from 25° to 40° brings about a small decrease in the magnitude of the exothermic heats of mixing for all these systems. The effect of increase in tempera-

TABLE 1 — HEATS OF MIXING AT 25° FOR VARIOUS BINARY SYSTEMS AS A FUNCTION OF MOLE FRACTION OF FIRST COMPONENT

x_1	H^E kJ mole^{-1}	H^E/x_1 kJ mole^{-1}	x_1	H^E kJ mole^{-1}	H^E/x_1 kJ mole^{-1}
	WATER-n-BUTYLAMINE			ETHANOL + n-BUTYLAMINE	
0·2373	−2·1481	−9·052	0·1504	−1·3180	−8·764
0·2972	−2·5235	−8·491	0 2752	−2·1350	−7·758
0·3285	−2·7467	−8·361	0 3506	−2·5463	−7·263
0·3973	−3·0317	−7·631	0·4041	−2·7366	−6·772
0·4954	−3·4011	−6·865	0·4741	−2·9532	−6·229
0·5797	−3·3960	−5·858	0·5744	−2·9587	−5·151
0·6635	−3·1110	−4·689	0·6137	−2·8854	−4·702
0·7676	−2·5778	−3·358	0·6831	−2·7364	−4·006
0·8212	−2·1230	−2·585	0·7214	−2·6246	−3·638
0·8916	−1·4271	−1·601	0·7552	−2·3775	−3·148
0·9615	−0·6758	−0·703	0·8138	−1·9415	−2·386
			0·8551	−1·6457	−1·925
			0·9226	−0·8507	−0·922
				1-BUTANOL + n-BUTYLAMINE	
			0·0778	−0·7506	−9·649
			0·1197	−1·0986	−9·178
			0·2106	−1·7991	−8·547
	METHANOL + n-BUTYLAMINE		0·2732	−2·1991	−8·050
			0·3320	−2·4602	−7·410
0·1883	−1·9498	−10·355	0·4549	−2·8629	−6·293
0·2043	−2·0284	−9·929	0·4984	−2·9054	−5·829
0·2929	−2·8613	−9·769	0·5158	−2·7883	−5·406
0·3399	−3·1226	−9·187	0·5784	−2·8887	−4·994
0·4329	−3·6666	−8·470	0·5970	−2·8304	−4·741
0·4746	−3·8066	−8·021	0·6516	−2·6598	−4·082
0·5411	−3·8603	−7·134	0·7039	−2·2866	−3·249
0·6402	−3·7650	−5·881	0·7767	−1·9471	−2·507
0·7348	−3·2700	−4·450	0·8385	−1·6407	−1·957
0·8205	−2·4715	−3·012	0·9220	−0·7488	−0·8121
0·8700	−1·9040	−2·189			
0·9242	−1·2302	−1·331			

TABLE 2 — VALUES OF THE CONSTANST OF EQ. (1) H^E_{max} AND CORRESPONDING VALUE OF x_1

System	Temp. °C	B kJ mole^{-1}	C kJ mole^{-1}	D kJ mole^{-1}	H^E_{max} kJ mole^{-1}	x_1 corresponding to H^E_{max}
Water + n-butylamine	25[a]	−13·800	−3·163	+3·172	−3·476	0·522
	40[b]	−13·342	−2·611	+2·546	−3·361	0·547
Methanol + n-butylamine	25[a]	−15·402	−3·534	+1·720	−3·900	0·555
	40[b]	−15·164	−3·570	+2·698	−3·834	0·556
Ethanol + n-butylamine	25[a]	−11·891	−2·146	+0·740	−2·995	0·545
	40[b]	−11·536	−1·891	+0·427	−2·901	0·551
1-Propanol + n-butylamine	25[c]	−12·275	−1·685	+3·469	−3·073	0·534
	40[b]	−11·329	−1·200	+1·406	−2·839	0·526
1-Butanol + n-butylamine	25[a]	−11·509	−0·566	+1·335	−2·879	0·512
	40[b]	−10·952	−1·372	+0·935	−2·747	0·531

(a) This work. (b) Reference 3. (c) Reference 1.

ture on H^E shows that $\partial H^E/\partial T = C^E_p$ is a positive quantity although small in magnitude for all these systems.

The only results already reported in the literature on the heats of mixing of the binary mixtures of n-butylamine with n-alcohols are those by Nakanishi et al.[5] for the n-butylamine + methanol system at 25° and 45°, by Murakami and Fujishiro[6] for n-butylamine + 1-butanol at 25° and by Ratkovics et al.[7] at 20° for the binary mixtures of n-butylamine with methanol, ethanol, 1-propanol and 1-butanol. Since the temperatures of measurements by various groups of workers are not always the same, a strict comparison of all the available literature data

amongst themselves and with our results is not possible. The experimental values of H^E for the different systems studied by us at 25° and 40° coupled with the assumption that the values of $\Delta H^E/\Delta T$ for this small temperature interval may be reasonably considered to be constant, leads us to the conclusion that a decrease in the temperature of experiment from 25° to 20° is expected to bring about an increase in the heats of mixing by $\leqslant 2\%$, a value very close to the limit of our experimental error in the measurements of the heats of mixing. It is, therefore, not unreasonable to compare the results of the heats of mixing of our experiments at 25° and those of Nakanishi et al.[5] at 25° and of
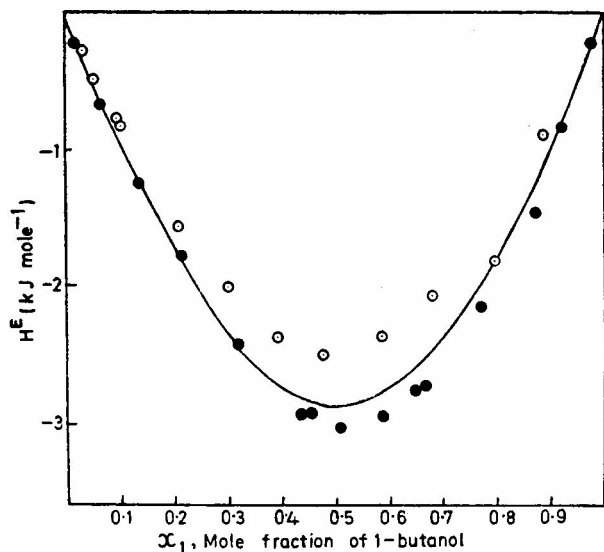
Fig. 1 — Heats of mixing of 1-butanol+n-butylamine system at 25° (———) present work; (○○○) data of Murakami and Fujishiro (●●●) data of Ratkovics et al.[7]

Murakami and Fujishiro[6] at 25° with those of Ratkovics et al. at 20°. There is a reasonably good agreement between our data at 25° and those of Ratkovics et al. at 20° for the binary system studied, except that in the 1-butanol mole fraction region of 0·4 to 1, the values of H^E observed by us are increasingly less exothermic than those reported by the Hungarian workers[7] (Fig. 1). However, the values of H^E reported by Nakanishi et al.[5] for n-butylamine + methanol system at 25° and by Murakami and Fujishiro[6] for n-butylamine+1-butanol system at 25° are 5 to 15% less exothermic than those found by us, the difference being much more marked for the latter system as shown in Fig. 1. The Japanese workers[5,6] in their studies have used the same twin-type calorimeter and checked its accuracy by determining the endothermic heats of mixing of benzene with carbon tetrachloride in contrast to the calibration procedure adopted by us[3]. We believe that the differences between our results and those of the Japanese workers[5,6] may be traced to the uncertainty in the calibration procedure adopted by them.

G^E at 40°C for the binary mixtures of n-butylamine + ethanol[4], n-butylamine + 1-propanol[4] and n-butylamine + 1-butanol[8] are negative throughout the concentration range. These values when plotted against mole fractions of the alcohols also fall on nearly symmetrical parabolic curves with maxima close to 0·5 mole fractions of the alcohols. The values of TS^E at 40° calculated from the relation $TS^E = H^E - G^E$ for the binary mixtures of n-butylamine with (C_2-C_4) n-alcohols are also negative throughout the concentration range. These values when plotted versus the mole fraction of the alcohols give similarly nearly symmetrical parabolic curves with maxima close to 0·5 mole fraction of the alcohols.

According to Ott et al.[9] and McKinnon and Williamson[10], the positive excess heat capacity C_p^E for a binary mixture shows the existence of a specific attractive interaction between the solute and the solvent molecules. The positive excess heat capacities for the binary mixtures of n-butyl amine with n-alcohols/water coupled with the pronounced exothermic heats of mixing, can, therefore, be taken as an evidence of complex formation between water/alcohol and n-butylamine molecules. The near symmetry of the H^E, TS^E and G^E curves and V^E curves (unpublished data, Pradhan, S. D. and Mathur, H. B.) with maxima at about $x = 0·5$, further suggests that interaction in all these cases is mainly of 1:1 type although the presence of more complicated interactions A_iB_j (A = alcohol, B = amine) cannot be ruled out. It is now well established that both the primary alcohols and primary amines exist in associated form in their pure state. The literature on the self-association of the alcohols[15-20] and the amines[21-25] in non-polar solvents presents a rather ill-defined picture and the problem of the composition of the self-associated species is still debatable. Hence any attempt to define the nature of the associated species in mixtures of n-butylamine with alcohols become more intractable. Despite the difficulties in the formulation of a specific model for the structure of the binary mixtures of n-alcohols with n-butylamine, it will still be useful to approach the problem of the alcohol-amine interaction from a purely thermodynamic standpoint without invoking beforehand any specific model for the structure of the binary liquid mixtures. The non-specific interactions of the binary mixtures of n-butylamine with (C_1-C_4) n-alcohols are expected to be very similar and small as compared to the strength and the number of hydrogen bonds formed in those mixtures. The pronounced exothermic effect accompanying the mixing of n-butylamine with water and the n-alcohols (C_1-C_4) observed in our experiments may be considered to arise as a net result of the following three heat effects:

(1) Endothermic effect, $\Sigma n_i\Delta H_i$, accompanying the breaking of alcohol-alcohol bonds on dilution of the self-associated alcohols, where n_i is the number of alcohol-alcohol bonds broken and ΔH_i is the heat associated with the breaking of each such bond.

(2) Endothermic effect, $\Sigma n_j\Delta H_j$, accompanying the breaking of amine-amine bonds on the dilution of self-associated n-butylamine, 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.

(3) Exothermic effect associated with the formation of alcohol-amine bonds, viz. $\Sigma n_{ij}\Delta H_{ij}$, where n_{ij} is the number of alcohol-amine bond and ΔH_{ij} is the heat associated with the formation of each such bond in the A_iB_j complexes.

Hence

$$-H^E = + \Sigma n_i\Delta H_i + \Sigma n_j\Delta H_j - \Sigma n_{ij}\Delta H_{ij} \qquad ...(2)$$

In order to estimate the hydrogen bond energy associated with the interaction of butyl amine with an alcohol we have made use of a thermochemical cycle shown in Fig. 2.

The hydrogen bond energy of the alcohol-amine complex is given by the enthalpy change in step (5)
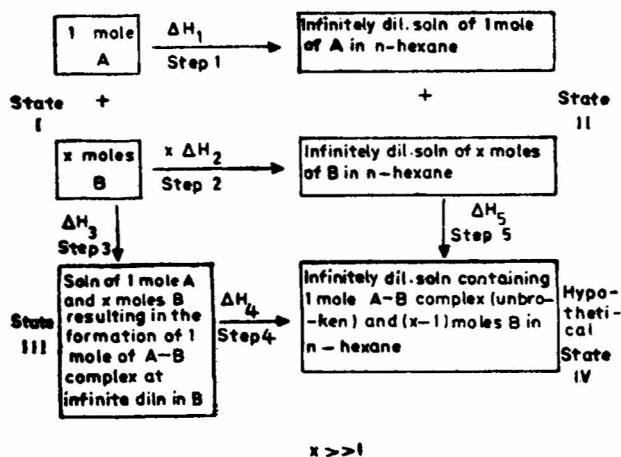
Fig. 2 — The thermochemical cycle

Fig. 3 — Heats of mixing $\Delta H^m/x_1 x_2$ of methanol+n-hydrocarbon systems as a function of the mole fraction x_1 of methanol [($\bigcirc\bigcirc\bigcirc$) methanol+n-hexane system at 20° from the data of Pahlke *et al.*[26]; ($\triangle\triangle\triangle$) methanol+$n$-hexane system at 25° from the data of Savini *et al.*[28]]

in which one mole of alcohol (A) at infinite dilution in n-hexane is mixed with x moles of amine (B) also at infinite dilution in n-hexane to give a hypothetical state-IV in which one mole of complex A-B and x moles of amine (B) are both present at infinite dilution in n-hexane. Hence the hydrogen bond energy is equal to the enthalpy change ΔH_5. This can be calculated from the thermochemical cycle, viz.

$$\Delta H_1 + x\Delta H_2 + \Delta H_5 = \Delta H_3 + \Delta H_4 \qquad ...(3)$$

where ΔH_1 and ΔH_2 are the enthalpies associated with the transfer of one mole of alcohol and one mole of amine respectively from their pure state to a state where each alcohol and each amine molecule is surrounded by a large number of n-hexane molecules, a state in which they can be said to be present in their monomeric state. ΔH_3 is the energy change associated with the transfer of one mole of alcohol from its pure alcohol state to a state where each alcohol molecule forms a hydrogen bond with a n-butylamine molecule and the alcohol-n-butylamine complex is surrounded by a large number of n-butylamine molecules. Two separate energy changes contribute to ΔH_4: (i) ΔH_4^{BH}, the heat of dilution of $(x-1)$ moles of n-butylamine by a large quantity of n-hexane which is equal to $(x-1)\Delta H_2$, and (ii) ΔH_4^d, the difference in the dipolar stabilization enthalpies of $A-B$ complex dipole arising from the reaction field of n-butylamine and n-hexane media. The Eq. (3) may, therefore, be rewritten as,

$$\Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + (x-1)\Delta H_2 + \Delta H_4^d$$
$$...(4)$$

or

$$\Delta H_5 = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d \qquad ...(5)$$

The value of ΔH_1 can be determined by plotting the values of H^E/x_1 or $H^E/x_1 x_2$ versus the mole fraction x_1 of the alcohol in the alcohol+n-hydrocarbon mixture and extrapolating to infinite dilution $(x_1 \to 0)$. Heats of mixing of the n-alcohols with normal aliphatic hydrocarbons have been determined by several workers[26-31]. The data of Pahlke *et al.*[26] and Van Ness and coworkers[28-30], are most suitable for such an extrapolation to an infinite

dilution of alcohol since the measurements of these authors, unlike the work of Brown *et al.*[31], have been made at very dilute concentrations of the alcohols.

A perusal of the work of Van Ness and coworkers[30] on the heats of mixing of ethanol + n-heptane systems in the dilute concentration range of the ethanol $(x_1 < 0.001)$ indicates that a rise of temperature from 10° to 30° is expected to bring about a decrease in the extrapolated value of the heat change $\Delta H_1 = \text{Lim}_{x_1 \to 0}(H^E/x_1 x_2)$ by about only 1%. Hence it is reasonable to take the value of $\text{Lim}_{x_1 \to 0} (H^E/x_1 x_2)$ at 20° or 30° equal to that at 25°. The work of Van Ness *et al.* further shows that the values of ΔH_1 determined from measurements at 30° for ethanol + n-hexane and ethanol + n-nonane are almost equal. Therefore, it will not be unreasonable to ignore any possible effect of the change of a hydrocarbon solvent from hexane to heptane on the value of $\Delta H_1 = \text{Lim}_{x_1 \to 0} (H^E/x_1 x_2)$. The plots of $H^E/x_1 x_2$ versus x_1 for the systems, methanol + n-hexane at 20° and 25°; ethanol + n-hexane at 20° and 30° and ethanol + n-heptane at 30°; and of 1-butanol + n-hexane at 20° and 1-butanol + n-heptane at 30° are shown in Figs 3-5 respectively. The nature of the curves shows that the self-association of the alcohols is quite significant even at very dilute concentrations. The heats of mixing per mole of alcohol at infinite dilution thus determined are summarized in Table 3. It may be noted that the value of $\Delta H_1 = \text{Lim}_{x_1 \to 0}(H^E/x_1 x_2)$ thus obtained for ethanol from the work of Pahlke *et al.* at 20° coincides with the value reported by Van Ness and coworkers[31] at 30°. We have, therefore, taken the
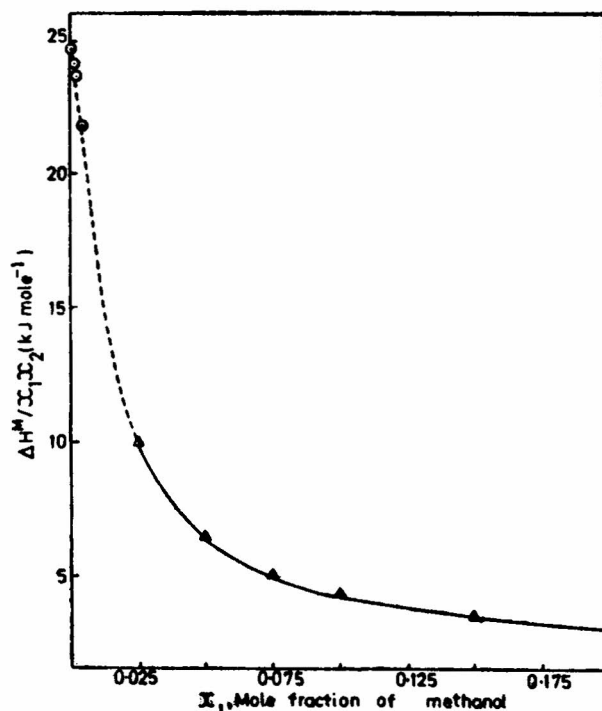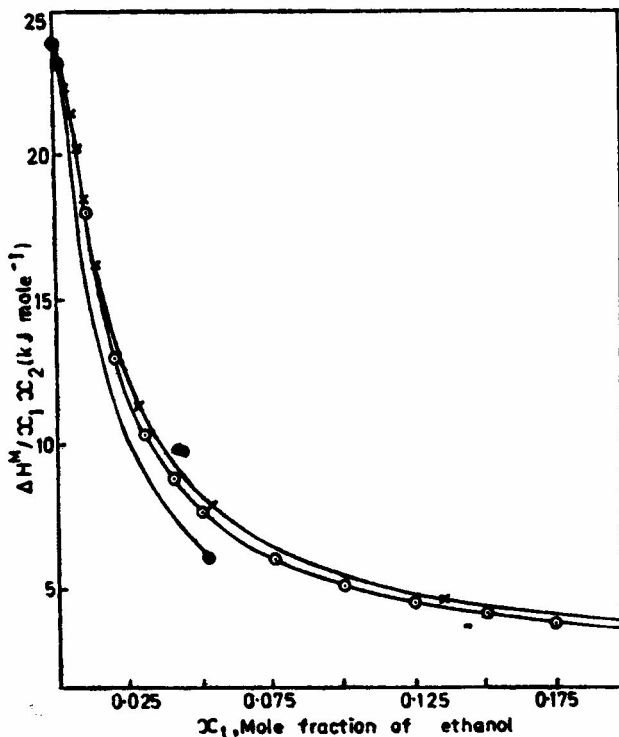
Fig. 4 — Heats of mixing $\Delta H^m/x_1 x_2$ of ethanol+n-hydrocarbon systems as a function of the mole fraction x_1 of ethanol [(●●●) ethanol+n-hexane system at 20°, from the data of Pahlke et al.[26]; (×××) ethanol-heptane system at 30°, data of Van Ness et al.[30] (○○○) ethanol+n-hexane system at 30° from the data of Savini et al.[29]]

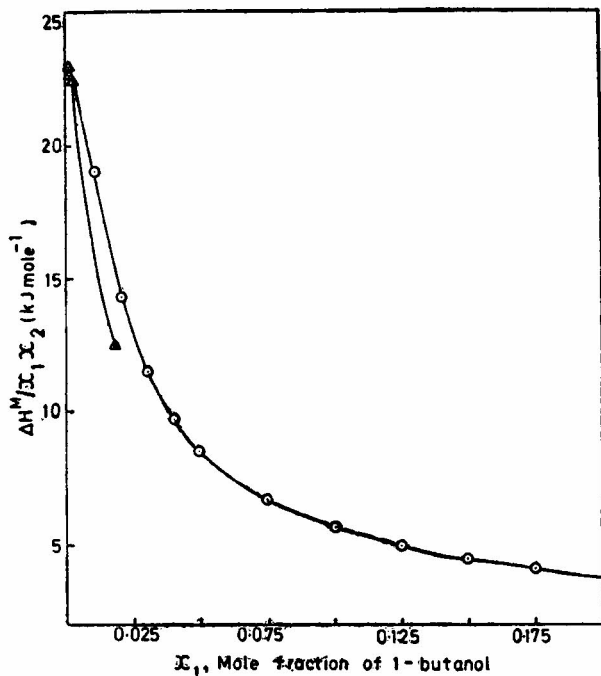

Fig. 5 — Heats of mixing $\Delta H^m/x_1 x_2$ of 1-butanol+n-hydrocarbon systems [(△△△) 1-butanol+n-hexane system at 20° from the data of Pahlke et al.[26]; (○○○) 1-butanol+n-heptane system at 30° from the data of Savini et al.[29]]

TABLE 3 — VALUES OF THE MOLAR ENTHALPIES OF TRANSFER OF ALCOHOL/AMINE FROM PURE STATE TO INFINITE DILUTION IN NORMAL HYDROCARBONS

Systems	$\Delta H_1 = \mathrm{Lim}_{x_1 \to 0}\ H^E/x_1 x_2$ (kJ mole^{-1}) at		
	20°	30°	35°
Methanol+n-hydrocarbons	+24·69*(a) (hexane)	—	—
Ethanol+n-hydrocarbon	+23·85*(a) (hexane) +21·09(e) (NMR in cyclohexane) +21·76(f) (NMR in CCl$_4$) +30·12(g) (NMR in CCl$_4$) +31·80(h) (IR in CCl$_4$)	+23·6(b) (heptane) —	— —
1-Propanol +n-hydrocarbon	+23·64*(a) (hexane)	+23·1±0·5(c) (heptane)	—
1-Butanol +n-hydrocarbon	+23·01*(a) (hexane)	+22·8±0·5(c) (heptane)	—
n-Butylamine +n-hydrocarbon	—	—	+5·3*(d)

(a) Ref. 26. (b) Ref. 30. (c) Ref. 29. (d) Ref. 6.
(e) Ref. 32. (f) Ref. 33. (g) Ref. 34. (h) Ref. 35.
*The values used for calculation in Eq. 5.

TABLE 4 — VALUES OF ΔH_3 FOR ALCOHOL/WATER (1) +n-BUTYL AMINE (2) BINARY MIXTURES

Systems	ΔH_3 (kJ mole^{-1})	Ref.
Water+n-butylamine	−10·4±1	This work
Methanol+n-butylamine	−11·2±1	do
Ethanol+n-butylamine	−9·5±1	do
1-Propanol+n-butylamine	−9·0±1	Ref. 1
1-Butanol+n-butylamine	−9·7±1	This work

$$\Delta H_3 = \mathrm{Lim}_{x_1 \to 0}\ H^E/x_1.$$

values of ΔH_1 at 25° (Table 3) to be equal to $\mathrm{Lim}_{x_1 \to 0}$ $(H^E/x_1 x_2)$ at 20° from the data of Pahlke et al.[26] for all the systems. It may be pointed here out that the values of ΔH_1 for different n-alcohols have also been determined by spectroscopic methods but the results obtained by different workers and by different techniques show large variations as shown in Table 3 for only ethanol as an example.

The value of ΔH_2 has been similarly estimated to be 5·3 kJ mole^{-1} by Murakami and Fujishiro[6]. We have obtained the value of ΔH_3 in Eq. (5) for the alcohol-n-butylamine systems (Table 4, Fig. 6) by plotting the values of H^E/x_1 versus the mole fraction x_1 of alcohol and extrapolating the curve to infinite dilution $(x_1 \to 0)$. We have avoided the customary plots of $H^E/x_1 x_2$ versus x_1, since our data showed a greater scatter in this form and hence made the extrapolation to infinite dilution more uncertain than in the plots of H^E/x_1 versus x_1. ΔH_4^d may be written as

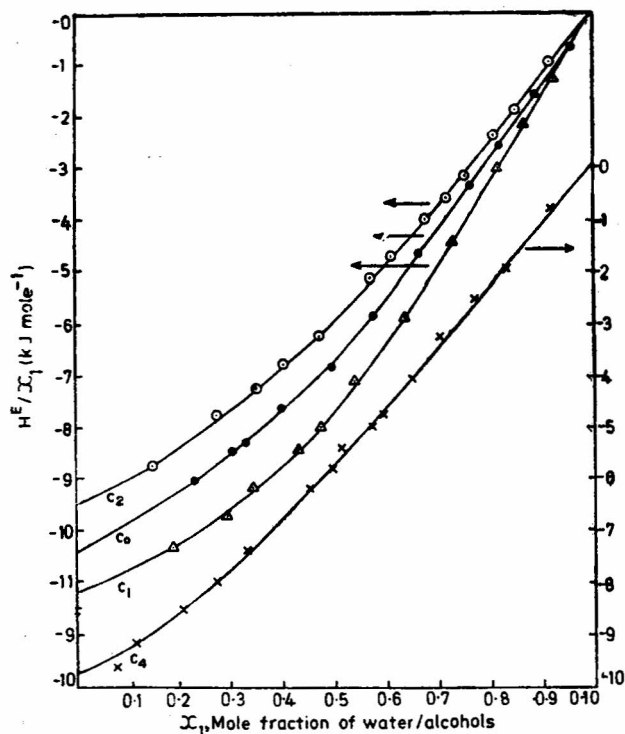$$\Delta H_4^d = \Delta H_H^d - \Delta H_B^d \qquad \ldots(6)$$

739

Fig. 6 — Heats of mixing H^E/x_1 of the binary mixtures of n-butylamine with water/alcohols at 25° as a function of x_1, the mole fraction of water/alcohol [Water $(C_0)+n$-butylamine system (●●●); methanol $(C_1)+n$-butylamine system (△△△); ethanol $(C_2)+n$-butylamine system (○○○) and 1-butanol $(C_4)+n$-butylamine system (× × ×)]

where ΔH_H^d and ΔH_B^d are the dipolar stabilization enthalpies of the alcohol-n-butylamine complex dipole arising from the reaction field of n-hexane and n-butylamine media respectively.

The dipolar stabilization enthalpies of a dipole in a medium i, can be calculated from the expression

$$\Delta H_i^d = \frac{\partial(\Delta G_i/T)}{\partial(1/T)} \qquad \text{...(7)}$$

where ΔG_i is the dipolar stabilization free energy of a dipole in the medium i. The value of ΔG_i is equal to the work done in bringing a polarizable dipole from an infinite distance outside to inside the dielectric medium. This can be considered to be divided into three parts: (i) The work W_1 required to enlarge the dipole, (ii) the work W_2 required to polarize the dielectric, and (iii) the work W_3 required to place the dipole in the reaction field R of the medium. Hence,

$$\Delta G_i = W = W_1+W_2+W_3 \qquad \text{...(8)}$$

$$= -\tfrac{1}{2}f\mu^2/(1-f\alpha) \quad \text{(ref. 36)} \qquad \text{...(9)}$$

where the value of f is given by the expression

$$f = \frac{2(\epsilon-1)}{a^3(2\epsilon+1)} \qquad \text{...(10)}$$

α, the polarizability, is given by the relation

$$\alpha = \frac{n^2-1}{n^2+2}a^3 \qquad \text{...(11)}$$

and ϵ and n are the dielectric constant and the internal refractive index respectively of the medium, a is the molecular radius of the dipole which can be calculated by an expression involving molecular weight M, Avogadro's number N and density d; viz.:

$$a^3 = \frac{3M}{4N\pi d} \qquad \text{...(12)}$$

The data necessary for the calculation of ΔG_i and hence of ΔH_A^d and ΔH_B^d are summarized in Table 5. The values of the densities, the refractive indices, and the dielectric constants are those from the Timmermans[37] and Landolf Bornstein[38] or derived from these values by interpolation.

Huysken et al.[39] have given the value of the dipole moment of 1-butylamine + 1-butanol 1:1 complex equal to 2.31×10^{-18} e.s.u. at 25°C. The dipole moment of (C_1-C_4) n-alcohols are nearly equal[40] and lie within the range 1.62-1.69 Debye. Hence it has been assumed that all the 1:1 n-butylamine-(C_1-C_4) n-alcohol complexes have the same value of the dipole moment and that this value does not change significantly between 15° and 25°. The molecular radii and the polarizabilities of the amine-alcohol complexes have been taken to be equal to the sum of the corresponding values of the component molecules. The values of ΔG_i and those of ΔH_H^d, ΔH_B^d and ΔH_A^d thus determined are summarized in Tables 6 and 7 for all the n-butylamine

TABLE 5 — VALUES OF THE CONSTANTS OF VARIOUS COMPONENTS USED FOR THE CALCULATION OF THE DIPOLAR STABILIZATION ENERGY OF THE ALCOHOL-n-BUTYLAMINE COMPLEXES

Temp. °C	Density (d)	Molecular radii $(a^3 \times 10^{23})$	Refractive index (n)	Polarizability $(\alpha \times 10^{23})$	Dielectric constant (ϵ)
METHANOL					
15	0.7961	1.593	1.3305	0.3254	—
20	0.7913	1.602	1.3287	0.3257	—
25	0.7865	1.612	1.3269	0.3261	—
ETHANOL					
15	0.7939	2.296	1.3633	0.5190	—
20	0.7894	2.309	1.3613	0.5112	—
25	0.7850	2.322	1.3593	0.5115	—
1-BUTANOL					
15	0.8133	3.607	1.4014	0.8771	—
20	0.8097	3.623	1.3991	0.8766	—
25	0.8060	3.639	1.3068	0.8760	—
n-BUTYLAMINE					
15	0.7484	3.868	—	0.9538	5.52
20	0.7440	3.890	—	0.9516	5.34
25	0.7395	3.914	—	0.9494	5.16
n-HEXANE					
15	—	—	—	—	1.897
20	—	—	—	—	1.890
25	—	—	—	—	1.883

$+ n$-alcohol complex dipoles. The enthalpy, ΔH_s, of the hydrogen bonds formed in the 1:1 complexes of n-butylamine with $(C_1\text{-}C_4)$ n-alcohols calculated from Eq. (5) are summarized in Table 8. It may

TABLE 6 — DIPOLAR STABILIZATION FREE ENERGY ALCOHOL-n-BUTYLAMINE COMPLEXES

Temp. (°C)	$\Delta G/T$ in	
	Amine medium	n-Hexane medium
METHANOL + n-BUTYLAMINE		
15	−9·315	−4·194
20	−8·975	−4·074
25	−8·644	−3·956
ETHANOL + n-BUTYLAMINE		
15	−8·261	−3·714
20	−7·979	−3·614
25	−7·679	−3·512
1-BUTANOL + n-BUTYLAMINE		
15	−6·819	−3·057
20	−6·597	−2·978
25	−6·376	−2·905

TABLE 7 — DIPOLAR STABILIZATION ENTHALPY OF ALCOHOL-n-BUTYLAMINE COMPLEXES

ΔH_H^d (kJ mole^{-1})	ΔH_B^d (kJ mole^{-1})	ΔH_4^d (kJ mole^{-1})
METHANOL + n-BUTYLAMINE		
−2·033	−5·733	+3·70
ETHANOL + n-BUTYLAMINE		
−1·748	−5·017	+3·27
1-PROPANOL + n-BUTYLAMINE		
−1·667	−4·667	+3·00
1-BUTANOL + n-BUTYLAMINE		
−1·290	−3·821	+2·53

TABLE 8 — ENTHALPY (ΔH_5) OF HYDROGEN BONDING BETWEEN n-BUTYLAMINE + $(C_1\text{-}C_4)$ n-ALCOHOLS ALONG WITH OTHER PUBLISHED VALUES

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

Systems	Enthalpy (ΔH_5) of hydrogen bonding at 25° (kJ mole^{-1})	Reference
Methanol + n-butyl-amine	−37·5 ± 2	Present work
Ethanol + n-butyl-amine	−35·4 ± 2	Present work
	−30·2	Calorimetry[13]
1-Propanol + n-butyl-amine	−35·0 ± 2	Calorimetry[1]
1-Butanol + n-butyl-amine	−35·5 ± 2	Present work
	−33·5	Colorimetry[6]
	−31·3	Calorimetry[43]
	−37·24	Vapour density[44] (at 70-100°C)

be observed that the increase in the chain length of the n-alcohols from C_1 to C_4 has practically no effect on the enthalpy of the hydrogen bond, and it can be considered to have a constant value of $35\cdot5 \pm 2$ kJ mole^{-1}. We have not been able to determine the strength of the water-n-butylamine hydrogen bond for want of accurate values of the enthalpy of the water-water bond. The solubility of water in an inert solvent like hydrocarbons or carbon tetrachloride, is too small to be measured by a calorimetric apparatus. In addition, there does not appear to be any agreement between the values of enthalpy of water-water bond determined by other experimental techniques[41,42].

The only results available in the literature on the enthalpy of hydrogen bond formation between n-butylamine and n-alcohols are those of Lambert and Huyskens[43] for n-butylamine + 1-butanol and n-butylamine + ethanol and of Cracco and Huyskens[44] and Murakami and Fujishiro[6] on n-butylamine + 1-butanol systems. These values are also given in Table 8 for comparison. It may be observed that there is good agreement between our results and those of Murakami and Fujishiro[6], while the agreement with the other data given in Table 7 is fair. Cracco and Huyskens's[44] value of 37·5 kJ mole^{-1} for the enthalpy of the hydrogen bond between n-butylamine and 1-butanol is for the vapour phase in the temperature range 70-100°. It has been observed that[45,46] the value of the energy of the bond formed in the vapour phase is usually higher than that formed in the liquid phase.

A perusal of the Table 3 shows that the decrease in the value of ΔH_1 with an increase in the chain length of $(C_1\text{-}C_4)$ alcohols is very small and that the strength of the hydrogen bond formed on the self-association of alcohols $(C_2\text{-}C_4)$ may be considered to have a constant value of $23\cdot5 \pm 0\cdot5$ kJ mole^{-1}. In the case of methanol, the enthalpy of the hydrogen bond has a sltghtly higher value of 24·7 kJ mole^{-1}. We have noted earlier that the strength of the hydrogen bond formed between n-butylamine and $(C_1\text{-}C_4)$ n-alcohols are also nearly equal. In spite of these results, significant differences in the heats of mixing H^E of n-butylamine with n-alcohols have been observed (Table 1). For example, the magnitude of the exothermic heats of mixing at 25° for an equimolar mixture of n-butylamine with water (C_0) and $(C_1\text{-}C_4)$ alcohols have the following decreasing order: (a) $C_1 > C_0 > C_3 > C_2 > C_4$ $[-H^E$ (kJ mole^{-1}) $3\cdot850 > 3\cdot450 > 3\cdot069 > 2\cdot973 > 2\cdot877]$ at 0·5 mole fraction of alcohol/water in amine-alcohol/water mixture. This order changes with temperature, as well as with the concentration, at a fixed temperature. It may be noted that the order of $|H^E|$ changes at 25° from that given in (a) above at 0·5 mole fraction of alcohol/water in the amine-alcohol/water mixtures to (b) $C_1 > C_0 > C_3 \simeq C_4 > C_2$ at 0·3 mole fraction of n-alcohol/water and to (c) $C_1 > C_0 > C_2 > C_3 > C_4$ at 0·7 mole fraction of n-alcohol/water.

A qualitative explanation for this change in the order of $|H^E|$ may be provided by a consideration of Eq. (2). We may consider, as an approximation that the values of $\Sigma n_j \Delta H_j$ make an almost equal contribution to $|H^E|$ at equivalent mole fractions of

alcohol/water for the mixtures of n-butylamine with $(C_1\text{-}C_4)$ n-alcohols or water. In addition, since the extent of the self-association and the heat of association of n-butylamine is small as compared to that in the $(C_1\text{-}C_4)$ n-alcohols and water, the magnitude of $\Sigma n_j \Delta H_j$ will be small as compared to $\Sigma n_i \Delta H_i$. The change in the order of the magnitude of the exothermic heats of mixing, as a function of temperature or mole fraction of alcohol/ water in the amine + alcohol/water mixture may, therefore, be primarily attributed to the varying changes of the dissociation of the alcohols with temperature/concentration. Brown et al.[31] as well as Gonzalez Posa et al.[47] have determined the heats of mixing of several n-alcohols with n-hexane at 25°, 35° and 45°. The plots of $\Delta H^m = \Sigma n_i \Delta H_i$ at 25° versus x_1, the mole fraction of alcohols, given by the latter group of workers indicate that the order of the endothermic heat of dilution $|\Delta H_m|$ of $(C_2\text{-}C_4)$ n-alcohols in hexane at 25°C is (d) $C_3 > C_4 > C_2$ at 0·3 mole fraction of alcohols; (e) $C_3 > C_2 > C_4$ at 0·5 mole fraction of alcohols; and (f) $C_2 > C_3 > C_4$ at 0·7 mole fraction of alcohols.

These changes in the order of $|\Delta H^m| = |\Sigma n_i \Delta H|$ shown in (d)-(f) above may be attributed to the difference in the number, n_i of the hydrogen bonds broken in the self-associated alcohols with n-hexane, since the strength of the hydrogen bonds in the self-associated $(C_1\text{-}C_4)$ n-alcohols is practically independent of the chain length (Table 3). Hence the observed changes in the order of $|H^E|$ for the n-butylamine—$(C_1\text{-}C_4)$ alcohol systems closely correspond to the order of $|\Delta H^m|$ for $(C_1\text{-}C_4)$ n-alcohols + n-hexane systems at equivalent mole fractions of the alcohols. For example, compare the orders (b) with (d); (a) with (e); and (c) with (f).

References

1. DUTTA CHOUDHURY, M. K. & MATHUR, H. B., *Indian J. Chem.*, **14A** (1976), 371.
2. COULSON, E. V., *Research*, **10** (1957), 429.
3. DUTTA CHOUDHURY, M. K. & MATHUR, H. B., *J. chem. Engng Data*, **19** (1974), 145.
4. DUTTA CHOUDHURY, M. K., *Indian J. Chem.*, **14** (1976), in press.
5. NAKANISHI, K., TOUHARA, H. & WATANABE, N., *Bull. chem. Soc. Japan*, **43** (1970), 2671.
6. MURAKAMI, S. & FUJISHIRO, R., *Bull. chem. Soc. Japan*, **39** (1966), 720.
7. RATKOVICS, F. & LASZLO', M., *Acta chim. scient. Hung.*, **79** (1973), 395.
8. RATKOVICS, F., LISZI, J. & LASZLO', M., *Acta chim. scient. Hung.*, **79** (1973), 387.
9. GOATES, J. R., SULLIVAN, R. J. & OTT, J. B., *J. phys. Chem.*, **63** (1959), 589.
10. McKINNON, I. E. & WILLIAMSON, A. G., *Aust. J. Chem.*, **17** (1964), 1374.
11. McGLASHAN, M. L. & RASTOGI, R. P., *Trans. Faraday Soc.*, **54** (1958), 496.
12. RENON, H. & PRAUSNITZ, J. M., *Chem. engng Sci.*, **22** (1967), 299.
13. RENON, H. & PRAUSNITZ, J. M., (erratum), *Chem. engng Sci.*, **22** (1967), 1891.
14. KRETSCHMER, C. B. & WIEBE, R., *J. chem. Phys.*, **22** (1954), 1697.
15. VENTHIEL, M., BECKER, E. D. & PIMENTAL, G., *J. chem. Phys.*, **27** (1957), 95.
16. SAUNDERS, M. & HYNE, J. B., *J. chem. Phys.*, **29** (1958), 253; 1319.
17. FLETCHER, A. N. & HELLER, C. A., *J. phys. Chem.*, **71** (1967), 3742.
18. FLETCHER, A. N. & HELLER, C. A., *J. phys. Chem.*, **72** (1968), 1839.
19. AVEYARD, R., BRISCOVE, B. J. & CHAPMAN, J., *J. chem. Soc. Faraday I*, (1973), 1772.
20. TUCKER, E. E., FARNHAM, S. B. & CHRISTIAN, S. D., *J. phys. Chem.*, **73** (1969), 3820.
21. LAMBERT, J. D. & STRONG, E. D. T., *Proc. R. Soc.*, **200A** (1950), 566.
22. FEENEY, J. & STUCLIFFE, L. M., *Proc. chem. Soc.*, (1961) 118.
23. WOLFF, H., HOPFNER, A. & HOPFNER, H. M., *Ber. der. Bunsen*, **68** (1964), 410.
24. SCHUG, J. C. & CHANG, W. E., *J. phys. Chem.*, **75** (1971), 938.
25. FEENEY, J. & STUCLIFFE, L. M., *J. chem. Soc.*, (1962), 1123.
26. PAHLKE, H., WOLF, J. & WAHAGE, K., *Z. physik. Chem. (Frank)*, **B28** (1935), 1.
27. ELBE, G. VON, *J. chem. Phys.*, **2** (1934), 73.
28. SAVINI, C. G., WINTERHALTER, D. R. & VAN NESS, H. C., *J. chem. Engng Data*, **10** (1965), 171.
29. SAVINI, C. G., WINTERHALTER, D. R. & VAN NESS, H. C., *J. chem. Engng Data*, **10** (1965), 168.
30. VAN NESS, H. C., SOCZEK, C. A. & KOCHAR, N. K., *J. chem. Engng Data*, **12** (1967), 346.
31. BROWN, I., FOCK, W. & SMITH, F., *Aust. J. Chem.*, **17** (1964), 1104.
32. CHANDLER, W. L. & DINIUS, R. H., *J. phys. Chem.*, **73** 1969), 1596.
33. VAN NESS, H. C., VAN WINKLE, J., RICHTOL, H. H. & HOLLINGER, H. B., *J. phys. Chem.*, **71** (1967), 1483.
34. HUGGINS, C. M., PIMENTAL, G. C. & SHOOLERY, J. N., *J. phys. Chem.*, **60** (1956), 1311.
35. LIDDEL, U. & BECKER, E. D., *Spectrochim. Acta*, **10** (1957), 70.
36. BOTTCHER, C. J. F., *Theory of electrolytic polarization* (Elsevier, Amsterdam), 1952, 139.
37. TIMMERMANS, J., *Physico-chemical constants of pure organic compounds*, Vol. II (Elsevier, Amsterdam), 1965, 251; 335.
38. LANDOLT BORNSTEIN, *Physikalisehe Chemischen Tabellen* (Springer, Berlin), 1936.
39. CLERBAUX, T., DUTERME, P., ZEEGERS-HUYSKENS, T. & HUYSKENS, P., *J. chim. Phys.*, **64** (1967), 1326.
40. SMYTH, C. P., *Dielectric behaviour and structure* (McGraw-Hill, New York), 1955, 301.
41. WALRAFEN, G. E., *J. chem. Phys.*, **40** (1964), 3249.
42. JOLICOEUR, C. & CABANA, A., *Can. J. Chem.*, **46** (1968), 567.
43. LAMBERT, D. L. & ZEEGERS-HUYSKENS, TH., *J. chim. Phys.*, **60** (1963), 435.
44. CRACCO, F. & HUYSKENS, P., *Bull. Soc. chim. Belg.*, **69** (1960), 255.
45. CHEVALIER, J. L., *J. chim. Phys.*, **66** (1969), 1453.
46. DAVIES, M., JONES, P., PATNAIK, D. & MOELWYN-HUGUES, E. A., *J. chem. Soc.*, (1951), 1249.
47. GONZALEZ POSA, C., NUNEZ, L. & VILLAR, E., *J. chem. Therm.*, **4** (1972), 275.