

## The chain length and isomeric effect of alcohol on the excess properties of amine-alcohol systems : Excess free energy of mixing, enthalpy of mixing and volume change on mixing\*

SHIRISH D PRADHAN

National Chemical Laboratory, Pune 411 008, India

MS received 10 December 1980 ; revised 2 April 1981

**Abstract.** The effect of change in alkyl chain and the branching of the alkyl chain of alcohol on the interactions with amine has been studied. For this purpose, the three excess properties, viz., free energy of mixing, enthalpy of mixing and volume change on mixing have been studied. The vapour liquid equilibrium of *n*-butylamine-1-propanol, -1-butanol, -2-propanol, -2-butanol systems were studied at 55°C. The four systems show negative deviation from Raoult's Law. The heats of mixing of *n*-butylamine with 2-propanol and 2-butanol determined at 25°C show that both the systems are strongly exothermic because of amine-alcohol complex formation. The volume change on mixing of the four earlier mentioned systems were determined at 25°C, and is found to be negative for all the four systems, with the maxima at 0.5 mol fraction. Increase in the alkyl chain length of alcohol does not change the excess properties while the branching of the alkyl chain considerably affects all the excess properties.

**Keywords.** Excess thermodynamic properties ; binary liquid mixtures ; amine-alcohol interactions ; isomeric effect ; enthalpy of mixing ; volume change.

### 1. Introduction

The branching of the alkyl chain of primary alcohols and amines causes a significant change in many physical and thermodynamic properties. It has been shown calorimetrically that the enthalpy of self-association of the four isomeric butylamines decreases as the branching of alkyl chain approaches the  $\alpha$ -carbon atom (Pradhan and Mathur 1978). Similarly it has been observed that the volume change on mixing and the enthalpy of butylamine-methanol complex differ due to the steric and electromeric effect of the substitution of methyl group in the alkyl chain of butyl amine (Pradhan and Mathur 1979; Pradhan 1979). In the present paper the results on the heats of mixing, free energy of mixing and volume change on mixing of binary mixtures of *n*-butylamine with 1-propanol, 2-propanol, 1-butanol and 2-butanol have been reported and the effect of chain length as well as branching of the alkyl chain has been discussed.

\* N.C.L. Communication No. 2711.

## 2. Experimental

### 2.1. Materials

1-Propanol (Reanal-Poland), 2-propanol (B.D.H.), 1-butanol (B.D.H.) and 2-butanol (B.D.H.) were twice fractionally distilled over NaOH-AgNO<sub>3</sub> mixture using a 1 m long column packed with glass helices. *n*-Butylamine was similarly purified over metallic sodium. All the compounds were dried by A-4 type molecular sieve.

### 2.2. Vapour liquid equilibrium

The vapour liquid equilibrium data at 55° C were obtained using a modified Jones-Colburn still. The experimental details are given in Pradhan (1979).

### 2.3. Heats of mixing

The heats of mixing data at 25° C were obtained using a modified twin-type calorimeter (Pradhan and Mathur 1978).

### 2.4. Volume change on mixing

The volume change on mixing at 25° C was determined by the density method using a Lipkins-type two-arm pycnometer (Pradhan 1979).

## 3. Results and discussion

All the results on free energy of mixing ( $\Delta G$ ) and volume change on mixing ( $\Delta V$ ) for *n*-butylamine (1)-1-propanol,-2 propanol,-1-butanol,-2-butanol (2) systems and that on the enthalpy of mixing ( $\Delta H$ ) of *n*-butylamine (1)-2-propanol and -butanol(2) systems were fitted in a Redlich-Kister equation of type

$$\Delta M = \sum_{n=1}^{n=4} A_n (1 - 2x)^{n-1}, \quad (1)$$

where  $\Delta M$  is the excess property,  $x$  is the mol fraction of *n*-butylamine and  $A_n$  is the constant. The values of the constants were obtained by the least square method using an ICL-1904 S computer and are reported in table 1 along with the standard deviation.

### 3.1. Free energy of mixing

The vapour liquid equilibrium data for *n*-butylamine (1)-1-propanol(2), -2-propanol(2), -1-butanol(2) and -2-butanol(2) are given in table 2 along with the activity coefficients and the excess free energy of mixing ( $\Delta G$ ). The thermodynamic consistency of the experimental data was checked by the Gibbs-Duhem equation and all the systems were found to be thermodynamically consistent within less than 3%.

**Table 1.** Redlich-Kister equation constants for various excess properties of binary mixtures of *n*-butylamine with 1-propanol, 2-propanol, 1-butanol and 2-butanol.

Excess property	System	A1	A2	A3	A4	Standard deviation
$\Delta G$	<i>n</i> -Butylamine + 1-propanol	-2967.3	-180.1	-802.4	2981.9	26
	<i>n</i> -Butylamine + 2-propanol	-2283.0	71.3	796.1	2373.8	15
	<i>n</i> -Butylamine + 1-butanol	-3121.8	57.3	1078.3	2204.2	43
	<i>n</i> -Butylamine + 2-butanol	-2940.0	210.3	685.0	1484.3	25
$\Delta H$	<i>n</i> -Butylamine + 2-propanol	-9981.0	41.5	359.6	963.0	71
	<i>n</i> -Butylamine + 2-butanol	-9006.7	-680.9	2220.3	2544.0	62
$\Delta V$	<i>n</i> -Butylamine + 1-propanol	-4.9632	0.0283	0.5822	0.5561	0.019
	<i>n</i> -Butylamine + 2-propanol	-3.5004	0.0442	0.7351	-0.1749	0.010
	<i>n</i> -Butylamine + 1-butanol	-4.7500	0.0433	0.6385	0.3608	0.009
	<i>n</i> -Butylamine + 2-butanol	-2.9336	0.0080	0.1159	-0.1189	0.004

**Table 2.** Vapour liquid equilibrium data for *n*-butylamine(1) -1-propanol(2), 2-propanol(2), -1-butanol(2) and -2-butanol(2) systems at 55°C.

Mole fraction of amine		<i>P</i> mm/Hg	$\gamma_1$	$\gamma_2$	$\Delta G$ (J/mol)
$x_1$	$y_1$				
<b>1-Propanol :</b>					
0.0000	0.0000	118.8	..	1.0000	..
0.0520	0.0523	112.4	0.3356	0.9462	-298
0.1407	0.1758	117.0	0.4263	0.9437	-462
0.2173	0.3108	122.0	0.5166	0.9044	-605
0.3169	0.4947	137.9	0.5375	0.8574	-681
0.4311	0.6755	159.5	0.7353	0.7679	-771
0.5127	0.7794	183.1	0.8203	0.6944	-761
0.6299	0.8826	221.0	0.9108	0.5852	-700
0.7841	0.9472	268.3	0.9495	0.5487	-463
0.9131	0.9829	318.2	1.0002	0.5183	-158
1.0000	1.0000	342.9	1.0000	..	..

Table 2. (contd.)

## 2-Propanol :

0.0000	0.0000	228.6	..	1.0000	..
0.0643	0.0354	220.1	0.3563	0.9931	-199
0.1512	0.1210	214.8	0.5048	0.9738	-343
0.2364	0.2331	212.9	0.6177	0.9361	-448
0.3197	0.3596	214.2	0.7091	0.8828	-531
0.4194	0.5110	223.2	0.7993	0.8226	-564
0.4926	0.6179	235.0	0.8660	0.7736	-548
0.6199	0.7738	259.3	0.9493	0.6736	-490
0.7293	0.8664	283.3	0.9858	0.6145	-388
0.8137	0.9204	313.6	1.0340	0.5834	-261
0.9158	0.9698	328.9	1.0530	0.5158	-23
1.0000	1.0000	342.9	1.0000	..	..

## 1-Butanol :

0.0000	0.0000	45.9	..	1.0000	..
0.1008	0.2127	53.8	0.2821	1.0240	-281
0.1898	0.4636	64.9	0.4717	0.9535	-540
0.2631	0.6108	78.2	0.5396	0.8966	-662
0.3364	0.7474	99.7	0.6472	0.8240	-750
0.4391	0.8557	131.7	0.7588	0.7326	-806
0.5144	0.9090	162.4	0.8465	0.6561	-792
0.6225	0.9477	203.5	0.9116	0.6052	-674
0.7263	0.9731	253.3	0.9947	0.5442	-445
0.7879	0.9808	278.8	1.0160	0.5364	-325
0.8250	0.9856	293.7	1.0270	0.5139	-259
0.8982	0.9920	321.0	1.0300	0.4706	-137
0.9208	0.9939	321.4	1.0200	0.5254	-107
1.0000	1.0000	342.9	1.0000	..	..

## 2-Butanol

0.0000	0.0000	107.4	..	1.0000	..
0.0698	0.0756	107.9	0.3471	0.9840	-206
0.1678	0.2356	110.0	0.4584	0.9404	-496
0.2689	0.4284	121.9	0.5757	0.8863	-645
0.3581	0.5966	140.7	0.6940	0.8212	-695
0.4342	0.7084	159.5	0.7691	0.7619	-709
0.5204	0.8030	183.0	0.8358	0.6972	-725
0.5993	0.8765	215.2	0.9265	0.6120	-662
0.6981	0.9275	250.5	0.9797	0.5549	-523
0.7894	0.9584	281.1	0.9995	0.5086	-389
0.8954	0.9815	316.6	1.0140	0.5116	-160
1.0000	1.0000	342.9	1.0000	..	..

The plot of  $\Delta G/x_1x_2$  vs  $x_1$  shows a linear relationship which is the condition for the applicability of the van Laar equation (van Ness 1964). The van Laar constants are given in table 3. The  $x$ - $y$  diagrams for all the four systems are shown in figure 1. The curves represent the values obtained by means of van Laar equation and the signs are the actual experimental points. It can be seen

Table 3. Van Laar constants for *n*-butylamine(1) 1-propanol, 2-propanol, 1-butanol, 2-butanol(2) systems at 55°C.

System	<i>A</i>	<i>B</i>	Standard deviation ( $\sigma$ )
<i>n</i> -Butylamine + 1-propanol	-0.5313	-0.3954	0.0055
<i>n</i> -Butylamine + 2-propanol	-0.5105	-0.2974	0.0022
<i>n</i> -Butylamine + 1-butanol	-0.6554	-0.4027	0.0043
<i>n</i> -Butylamine + 2-butanol	-0.6210	-0.3382	0.0056

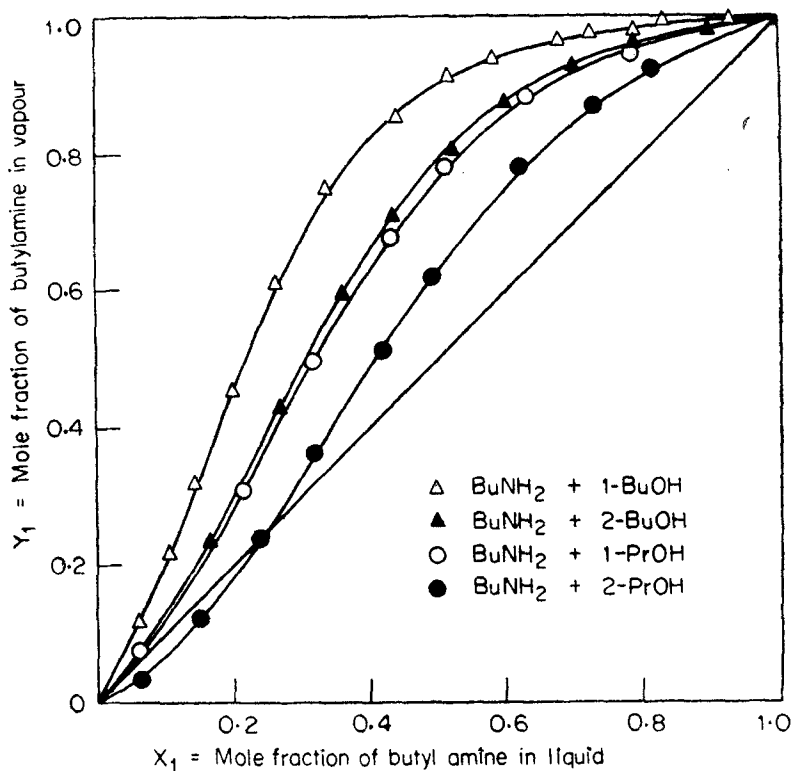


Figure 1. The *x*-*y* diagrams for *n*-butylamine-1-propanol(2), -1-butanol(2), -2-propanol(2) and 2-butanol(2) systems at 55°C.

that these systems can be represented by the van Laar equation with a good accuracy. At low mol fractions of butylamine ( $< 0.3$ ) the interaction between amine and alcohol appears to be stronger. The *x*-*y* diagram for 2-propanol system is a S-type curve and it forms an azeotrope nearly at 0.25 mol fraction of butylamine. The 1-propanol system forms a tangential azeotrope below 0.05 mol

fraction of amine. From the  $x$ - $y$  diagram of 2-butanol system it appears that the tangential azeotrope may be forming below 0.03 mole fraction of amine while the 1-butanol system does not form azeotrope with butylamine.

The excess free energy of mixing ( $\Delta G$ ) as a function of mol fraction of butylamine ( $x_1$ ) has been represented in figure 2. The line represents the curve obtained by equation (1) while the signs are the experimental points. The  $\Delta G$  is negative throughout the entire concentration range suggesting a strong interaction between the amine and alcohol molecules. The maximum free energy of mixing is observed at 0.45 mol fraction of butylamine for all the four systems and they exhibit the following trend

$$\begin{array}{cccc} 1\text{-BuOH} & > & 1\text{-PrOH} & > & 2\text{-BuOH} & > & 2\text{-PrOH} \\ (-790 \text{ J/mol}) & & (-755 \text{ J/mol}) & & (-725 \text{ J/mol}) & & (-560 \text{ J/mol}) \end{array}$$

Increase in the chain length has a negligible (about 2%) effect on the free energy of mixing while the branching of the alkyl chain causes a significant decrease in  $\Delta G$ . Substitution of one methyl group at  $\alpha$ -carbon atom as in the case of 2-butanol, decreases the  $\Delta G$  by about 8% compared to that of 1-butanol while the substitution of two methyl groups at  $\alpha$ -carbon atom as in the case of 2-propanol decreases the free energy by about 24% compared to that of 1-propanol.

### 3.2. Enthalpy of mixing

The results on the heats of mixing of  $n$ -butylamine with 2-propanol and 2-butanol are given in table 4. The heats of mixing are negative throughout the concentration range. The  $\Delta H$  as a function of mol fraction of butylamine ( $x_1$ ) is represented in figure 3. For ready comparison the data on the heats of mixing

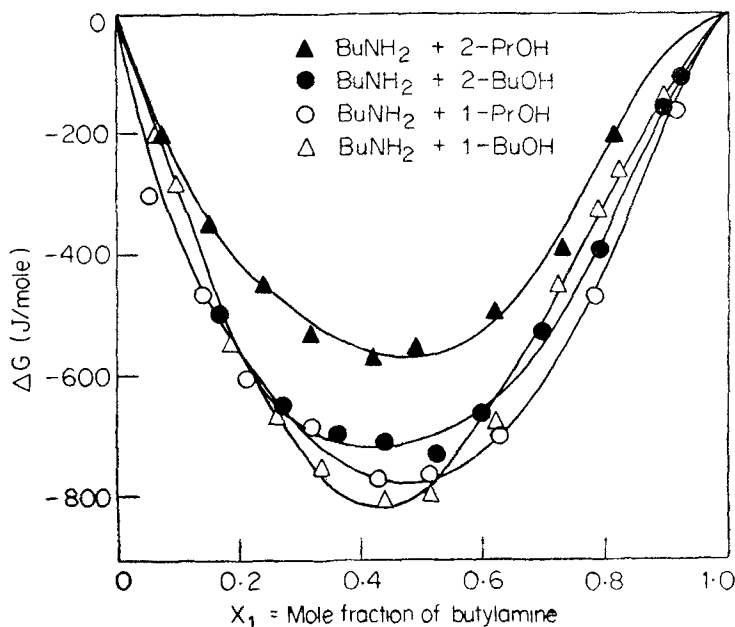


Figure 2. The  $\Delta G$  versus  $x_1$  curves for  $n$ -butylamine(1)-1-propanol(2), -1-butanol(2), -2-propanol(2) and -2-buanol(2) systems at 55°C.

Table 4. Enthalpy of mixing of *n*-butylamine(1) 2-propanol(2), -2-butanol(2) systems at 25° C.

Mol fraction of amine ( $x_1$ )	$\Delta H$ (J/mol)	Mol fraction of amine ( $x_1$ )	$\Delta H$ (J/mol)
2-Propanol		2-Butanol	
0.0985	-927	0.1008	-760
0.2056	-1626	0.1995	-1310
0.3000	-1991	0.2955	-1797
0.3475	-2311	0.4000	-2102
0.4028	-2389	0.5128	-2246
0.5016	-2595	0.5974	-2135
0.5974	-2506	0.6007	-2122
0.6984	-2099	0.6927	-1835
0.7495	-1760	0.8006	-1380
0.7987	-1406	0.8750	-960
0.9010	-875	0.9533	-193

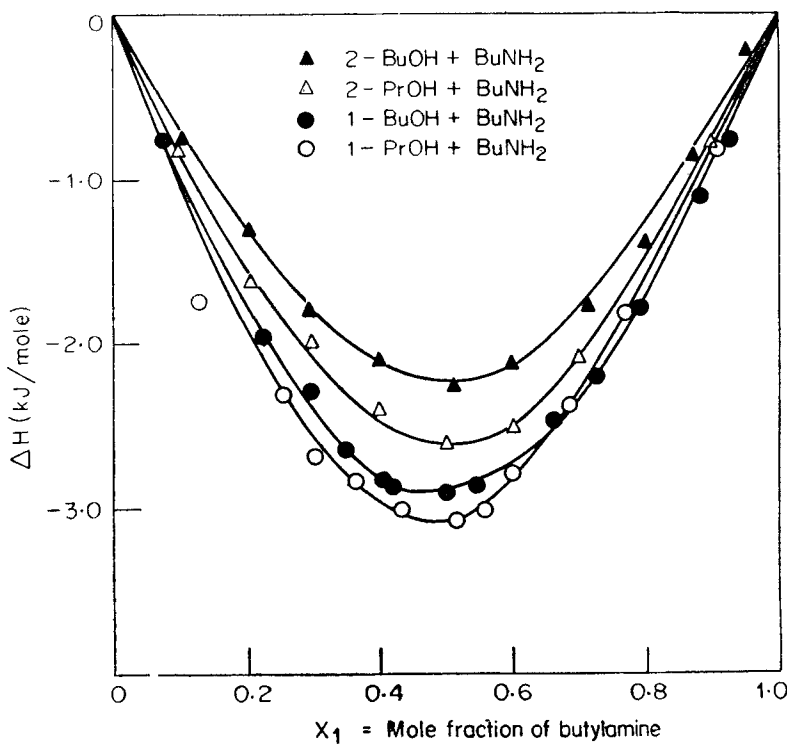


Figure 3. The  $\Delta H$  versus  $x_1$  curves for *n*-butylamine(1)-1-propanol(2), -1-butanol(2), 2-propanol(2) and -2-butanol(2) systems at 25° C.

of *n*-butylamine with 1-propanol and 1-butanol obtained by Dutta Choudhury and Mathur (1976) are presented in the same figure. The maximum heat of mixing is observed at 0.5 mol fraction for all the four systems.

It is well established that the amine and alcohol form essentially 1:1 type of complexes in their mixtures (Huysken *et al* 1960; Lambert *et al* 1963). In the present systems the  $\Delta H$  versus  $x_1$  as well as  $\Delta V$  versus  $x_1$  curves (see figure 4) are symmetrical with maxima at 0.5 mol fraction. It will therefore be reasonable to assume that 2-propanol and 2-butanol also form essentially 1:1 type of complex with butylamine.

The enthalpy of mixing for these four systems shows the following trend

1-PrOH	> 1-BuOH	> 2-PrOH	> 2-BuOH
(-3.1 kJ/mol)	(-2.9 kJ/mol)	(-2.6 kJ/mol)	(-2.25 kJ/mol)

Similar to  $\Delta G$ , the change in chain length has only a small effect (about 6%) on the enthalpy of mixing and the branching of the alkyl chain has a large effect on the enthalpy of mixing. However, unlike the trend in  $\Delta G$ , the substitution of one methyl group at the  $\alpha$ -carbon atom of alcohol as in 2-butanol reduces the

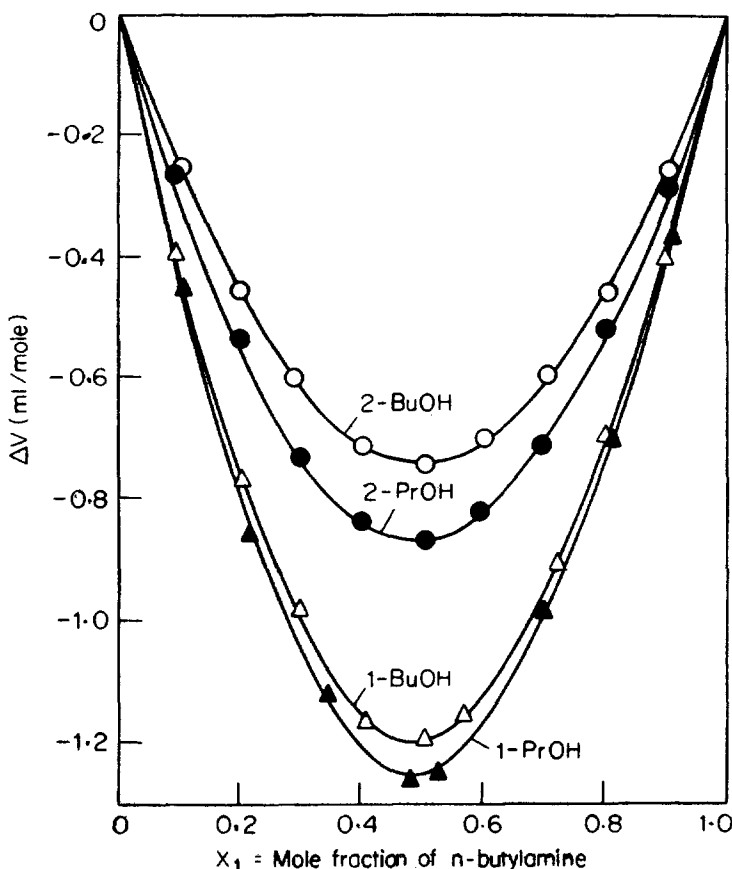


Figure 4. The  $\Delta V$  versus  $x_1$  curves for *n*-butylamine-(1)-1-propanol(2), -1-butanol(2), -2-propanol(2) and -2-butanol(2) systems at 25°C.



magnitude of  $\Delta H$  to a larger extent (about 24%) than that observed in the two methyl groups substituted alcohol (about 16%) compared to corresponding straight chain alcohol.

The  $\Delta H$  value obtained at particular mol fraction ( $x$ ) is essentially the net effect of the three thermal processes, viz.

(i) endothermic effect of breaking of the self-associated alcohol polymers by amine ;

(ii) endothermic effect of breaking of the self-associated amine molecules by alcohol ;

(iii) exothermic effect of alcohol-amine complex formation. The enthalpy of mixing at a particular mol fraction ( $x$ ) will be

$$\Delta H_m = \Sigma n_i \Delta H_1 + \Sigma n_j \Delta H_2 + \Sigma n_{ki} \Delta H_3 \quad (2)$$

where  $n_i$  and  $n_j$  are the number of hydrogen-bonded alcohol-alcohol and amine-amine molecules broken,  $n_{ki}$  is the number of amine-alcohol complex molecules formed and  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  are the enthalpies of self-association of alcohol, amine and complex formation respectively.

The enthalpy of complex formation ( $\Delta H_c$ ) is calculated by means of the thermochemical cycle which detailed in Pradhan and Mathur (1979). The ultimate equation to obtain the enthalpy of complex formation is

$$\Delta H_c = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d \quad (3)$$

where  $\Delta H_1$  and  $\Delta H_2$  are the partial molar enthalpies of mixing of alcohol and amine in a non-polar solvent,  $\Delta H_3$  is the partial molar enthalpy of amine in alcohol and  $\Delta H_4^d$  is the dipolar stabilisation energy of the complex. The values of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  are obtained by extrapolating the  $\Delta H/x_1x_2$  versus  $x_1$  curves to zero mol fraction.

The dipole moment of the complex is required for the calculations of dipolar stabilisation energy. The dipole moments of *n*-butylamine-2-propanol and *n*-butylamine-butanol are not available in literature. The dipole moment of *n*-butylamine-1-butanol is reported to be 2.31 D (Clerbaux *et al* 1967). Considering that the dipole moments of 1-butanol, 2-propanol and 2-butanol are close to each other and the thermochemical cycle calculations are based on the assumption of 1:1 complex formation, it will be reasonable to accept the dipole moments of 2-propanol and 2-butanol complexes to be 2.31 D. This assumption may cause a slight error in the  $\Delta H_4^d$  value but considering that the contribution of  $\Delta H_4^d$  to  $\Delta H_c$  is small (< 10%) the error can be neglected. The  $\Delta H_4^d$  is calculated as explained in Pradhan and Mathur (1979). The uncertainty in the value of  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta H_3$  and  $\Delta H_4^d$  is of the order of 0.2-0.3 kJ, 0.5 kJ, 0.5-0.7 kJ and 0.5 kJ respectively, so that the overall uncertainty in the value of  $\Delta H_c$  is of the order of  $\pm 1.5$  to 2.0 KJ/mol.

It may be seen from table 5 that the enthalpies of complex formation of 1-propanol, 1-butanol and 2-butanol are nearly equal. Considering the homologous character of 1-propanol and 1-butanol the  $\Delta H_c$  values for these two complexes are expected to be nearly the same. In the case of 2-butanol complex, a methyl group at the  $\alpha$ -carbon atom introduces two opposing effects on the amine-alcohol interaction. Firstly a steric effect which decreases the strength of complex and

secondly a electromeric effect which increases the electron density at O atom and consequently the strength of O-H...NH<sub>2</sub> hydrogen bonded complex is increased. From the value of  $\Delta H_c$  it appears that in the case of 2-butanolamine complex these two effects cancel each other. The  $\Delta H_c$  for 2-propanol-amine complex is larger than the remaining three complexes. It appears that because of the two methyl groups at  $\alpha$ -carbon, the electromeric effect dominates over the steric effect. It may be seen from table 5 that the enthalpy of self-association of 2-propanol is also higher than that of 1-propanol. The dominance of electromeric effect over steric effect was also observed by Geisler *et al* (1971) in the interactions between isomeric butanol with 1-butanol. Similarly in the case of interaction between methanol and four isomeric butylamines, the enthalpy of tertiary butylamine-methanol complex was found to be maximum (Pradhan and Mathur 1979).

The enthalpies of complex formation for 1-propanol, 1-butanol and 2-butanol are close to each other but the  $\Delta H$  values for 2-butanol systems are much less than those of 1-propanol and 1-butanol systems. Similarly the  $\Delta H_c$  for 2-propanol, complex is higher than the other three complexes but the  $\Delta H$  curve shows a significant decrease in  $\Delta H$  values compared to 1-propanol and 1-butanol systems. As explained earlier the  $\Delta H$  values at a particular mol fraction is the net effect of two endothermic and one exothermic effects. Since the values of  $\Delta H_1$  and  $\Delta H_2$  are nearly the same for all the systems and the ultimate value of  $\Delta H$  is negative, the magnitude of  $\Delta H$  will be governed essentially by the third term of equation (2) viz.,  $\sum n_{ki} \Delta H_c$ . The lower values of  $\Delta H$  for 2-propanol and 2-butanol systems may therefore be attributed to the formation of lesser number of amine-alcohol pairs in mixture. This assumption is further substantiated by the volume change on mixing of these systems.

### 3.3. Volume change on mixing

The results on the volume change on mixing of 1-propanol, 2-propanol, 1-butanol and 2-butanol systems have been given in table 6. In the case of binary mixtures

Table 5. Enthalpy of *n*-butylamine-alcohol complex formation by means of thermochemical cycle.

System	$\Delta H_1$ KJ/mol	$\Delta H_2$ KJ/mol	$\Delta H_3$ KJ/mol	$\Delta H_4^d$ KJ/mol	$\Delta H_c$ KJ/mol
1-Propanol + <i>n</i> -heptane	23.1 <sup>(a)</sup>	..	..	..	..
2-Propanol + <i>n</i> -heptane	25.4 <sup>(b)</sup>	..	..	..	..
1-Butanol + <i>n</i> -heptane	22.8 <sup>(a)</sup>	..	..	..	..
2-Butanol + <i>n</i> -hexane	23.9 <sup>(c)</sup>	..	..	..	..
1-Propanol + <i>n</i> -butylamine	..	-9.0 <sup>(d)</sup>	..	3.0 <sup>(d)</sup>	-37.6
2-Propanol + <i>n</i> -butylamine	..	-10.8	..	2.0	-42.7
1-Butanol + <i>n</i> -butylamine	..	-9.7 <sup>(e)</sup>	..	2.5 <sup>(d)</sup>	-38.5
2-Butanol + <i>n</i> -butylamine	..	-8.4	..	1.7	-39.1
<i>n</i> -Butylamine + <i>n</i> -hexane	..	..	8.5 <sup>(e)</sup>	..	..

<sup>(a)</sup> Savini *et al* (1965); <sup>(b)</sup> Van Ness *et al* (1967); <sup>(c)</sup> Brown *et al* (1969); <sup>(d)</sup> Datta Choudhury and Mathur (1976); <sup>(e)</sup> Pradhan and Mathur (1979).

Table 6. Volume change on mixing of *n*-butylamine with 1-propanol, 2-propanol 1-butanol and 2-butanol at 25°C.

$x_1$ mol fraction of amine	$d_{12}$ g/ml density of mixture	$\Delta V$ (ml/mol)
<i>1-Propanol</i>		
0.0000	0.79960	..
0.1074	0.79500	-0.46
0.2187	0.78969	-0.85
0.3467	0.78250	-1.11
0.4805	0.77362	-1.26
0.5280	0.77017	-1.24
0.7007	0.75652	-0.97
0.8103	0.74767	-0.69
0.9098	0.73957	-0.36
1.0000	0.73216	..
<i>2-Propanol</i>		
0.0000	0.78093	..
0.0978	0.77784	-0.26
0.1997	0.77413	-0.53
0.3002	0.77028	-0.73
0.4001	0.76581	-0.84
0.5020	0.76079	-0.87
0.5961	0.75578	-0.82
0.6954	0.75026	-0.71
0.7984	0.74418	-0.52
0.9027	0.73802	-0.27
1.0000	0.73220	..
<i>1-Butanol</i>		
0.0000	0.80580	..
0.0958	0.80159	-0.390
0.2037	0.79631	-0.76
0.2975	0.79100	-0.97
0.4075	0.78397	-1.16
0.5055	0.77680	-1.19
0.5670	0.77188	-1.15
0.7237	0.75846	-0.90
0.8031	0.75114	-0.69
0.8958	0.74240	-0.39
1.0000	0.73234	..
<i>2-Butanol</i>		
0.0000	0.80244	..
0.1006	0.79704	-0.25
0.1987	0.79142	-0.45
0.2882	0.78605	-0.60
0.4021	0.77867	-0.71
0.5032	0.77170	-0.74
0.6025	0.76436	-0.70
0.7048	0.75647	-0.60
0.8043	0.74863	-0.46
0.9048	0.74036	-0.25
1.0000	0.73225	..

**Table 7.** Maximum volume change on mixing and partial excess volumes of *n*-butylamine + 1-propanol, 2-propanol, 1-butanol and 2-butanol systems.

System	$\Delta V_{\max}$ ml/mol	$\Delta V_1$ ml/mol	$\Delta V_2$ ml/mol
<i>n</i> -Butylamine + 1-propanol	-1.250	-4.7	-4.20
<i>n</i> -Butylamine + 2-propanol	-0.866	-3.5	-4.20
<i>n</i> -Butylamine + 1-butanol	-1.189	-4.4	-4.1
<i>n</i> -Butylamine + 2-butanol	-0.738	-2.8	-3.2

of associated liquids such as amine-alcohol, it is not possible to apply any of the models based on the physical interactions as the effect of complex formation due to hydrogen bonding is much more pronounced than that of physical interaction (Battino 1971). However in such cases the volume change on mixing gives qualitative information regarding the molecular packing or arrangement in the bulk. The volume change on mixing ( $\Delta V$ ) as a function of the mol fraction of butylamine has been represented in figure 4. The  $\Delta V$  are negative throughout the concentration range and the maxima are nearly at 0.5 mol fraction which indicates the possibility of 1:1 type complex formation. The maximum excess volume ( $\Delta V_{\max}$ ) and the excess partial volumes of butylamine ( $\Delta V_1$ ) and alcohol ( $\Delta V_2$ ) are given in table 7. The  $\Delta V$  of these systems show the following trend

$$1\text{-propanol} > 1\text{-butanol} > 2\text{-propanol} > 2\text{-butanol}.$$

There is only a little difference in the excess volume functions of the two homologous alcohols. However, as observed in the other two excess properties, branched alcohols show a distinct effect on volume change. Substitution of one methyl group reduces the magnitude of  $\Delta V$  by about 40% whereas introduction of two methyl groups at  $\alpha$ -carbon atom reduces the magnitude of  $\Delta V$  by about 30% compared to their corresponding normal alcohols.

In the case of binary mixtures of amine and alcohol where the negative excess volume is due to the hydrogen bonded complex formation the magnitude of the excess volume would depend essentially on the number of complex pairs formed in the mixtures. From the trend on volume change, the number of complex pairs formed in different systems would be

$$1\text{-propanol} > 1\text{-butanol} > 2\text{-propanol} > 2\text{-butanol}.$$

This trend is consistent with the results on the heats of mixing of these systems.

#### 4. Conclusions

From the study on the excess free energy of mixing, enthalpy of mixing and volume change on mixing of the binary mixtures of 1-propanol, 2-propanol, 1-butanol and 2-butanol with *n*-butylamine the following conclusions may be drawn:

(i) All the systems have a strong interaction due to hydrogen bonding and form 1:1 type of complexes in the mixture.

(ii) Alcohol-amine systems form an azeotrope which depends on the boiling point of the alcohol. As the difference in the boiling points of alcohol and amine increases the tendency of azeotrope formation reduces.

(iii) Increase in the alkyl chain of normal alcohol does not make much change in any of the excess properties while the branching of the alkyl chain makes a significant change in all the excess properties.

(iv) Substitution of one methyl group at the  $\alpha$ -carbon atom does make much change in the strength of amine-alcohol complex compared to that of normal alcohol complex. The substitution of two methyl groups at the  $\alpha$ -carbon atom increases the strength of the amine-alcohol complex due to the electromeric effect.

(v) The extent of the amine-alcohol interaction is governed by the shape of molecules. The interaction is more in the case of linear molecules and decreases as the molecular symmetry is distorted.

## References

- Battino 1971 *Chem. Rev.* **71** 5  
Brown I, Fock W and Smith F 1969 *J. Chem. Thermodyn.* **1** 273  
Clerbaux T, Duterme P, Zeegers-Huyskens and Huyskens P 1967 *J. Chim. Phys.* **64** 1326  
Dutta Choudhury M K and Mathur H B 1976 *Indian J. Chem.* **A14** 735  
Geisler G, Fruwert J and Seidel H 1971 *Spectrochim. Acta* **A27** 1897  
Huysken S, Zeegers Th and Huyskens P 1960, *Bull. Soc. Chim. Belg.* **69** 267  
Lambert L and Huyskens and Zeegers Th 1963 *J. Chem. Phys.* **60** 435  
Pradhan S D 1979 *Proc. Indian Acad. Sci. (Chem. Sci.)* **A88** 47  
Pradhan S D 1979 *Indian J. Technol.* **17** (8) 324  
Pradhan S D and Mathur H B 1978 *Proc. Indian Acad. Sci. (Chem. Sci.)* **A87** 23  
Pradhan S D and Mathur H B 1979 *Proc. Indian Acad. Sci. (Chem. Sci.)* **A88** 337  
Savini C G, Winterhalter D R and Van Ness H C 1965 *J. Chem. Eng. Data* **10** 171  
Van Ness H C 1964 *Classical thermodynamics of non-electrolyte solution* (Oxford: Pergamon Press) 126  
Van Ness H C, Soczek C A, Peloquin G L and Machado R L 1967 *J. Chem. Eng. Data* **12** 277