

## Enthalpy of hydrogen bonded alcohol-butyl amine complexes by a simpler calorimetric method\*

SHIRISH D PRADHAN and GOPAL PATHAK

National Chemical Laboratory, Pune 411 008, India

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**Abstract.** The heats of mixing of *n*-butyl amine with methanol and *n*-propanol have been determined at 30° C and the enthalpies of alcohol-amine complex formation have been calculated by thermochemical cycle. The enthalpies of complex formation of butyl amine with methanol and *n*-propanol were found to be  $-44.3$  kJ/mole and  $-39.4$  kJ/mole respectively. The heats of mixing of synthetically prepared 1 : 1 molar mixtures of *n*-butyl amine with methanol, ethanol and *n*-propanol with *n*-hexane have also been determined at 30° C. The enthalpy of amine-alcohol complexes was obtained from the partial molar heats of dissociation of the complexes in *n*-hexane. The values agree with those obtained by the thermochemical cycle method.

**Keywords.** Heats of mixing ; butyl amine ; methanol ; ethanol ; propanol ; enthalpy of complexes.

### 1. Introduction

It has been well established that primary amines and alcohols form hydrogen bonded complexes in their mixtures and the complex formation is essentially 1 : 1 type (Lambert and Huyskins 1963 ; Cracco and Huyskins 1960 ; Huyskins 1960). The enthalpy of amine-alcohol complex for butyl amine with different alcohols (Duttachoudhury and Mathur 1976) and of isomeric butyl amines with methanol (Pradhan and Mathur 1979) obtained from thermochemical cycle, has earlier been reported from this laboratory. The ultimate equation for obtaining the enthalpy of complex formation ( $\Delta H_o$ ) from the thermochemical cycle method is

$$\Delta H_o = - \Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d \quad (1)$$

where  $\Delta H_1$  and  $\Delta H_2$  are the enthalpies of self-association of alcohol and amine,  $\Delta H_3$  is the partial molar enthalpy of amine in the amine-alcohol system and  $\Delta H_4^d$  is the dipolar stabilisation energy. The  $\Delta H_1$  and  $\Delta H_2$  values are obtained by extrapolating the  $\Delta H/x_1x_2$  versus  $x_1$  curves to zero concentration of alcohol

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and amine in the non-polar solvent. The  $\Delta H_3$  value is obtained by extrapolating  $\Delta H/x_1x_2$  versus  $x_1$  curve to zero concentration of amine for the amine-alcohol system. In order to get the enthalpy of amine-alcohol complex by this method, it is necessary to determine the heats of mixing for three systems, viz., alcohol + non-polar solvent, amine + non-polar solvent and amine + alcohol and in addition to this, data for dipolar stabilisation energy are also required. Thus, this method is laborious and there is a chance of considerable uncertainty in the values of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$ , unless the heats of mixing data are obtained at very dilute concentrations. It has been shown by Savini *et al* (1965) that in the case of associated liquids the  $\Delta H/x_1x_2$  value changes very rapidly in the dilute concentration range. It was considered worthwhile to obtain the enthalpy of complex formation directly by measuring the heats of dissociation of synthetically prepared 1 : 1 complex. In this paper we present the heats of mixing of *n*-butyl amine with methanol and *n*-propanol and that of amine-alcohol ( $C_1$  to  $C_3$ ) complexes with *n*-hexane in the concentration range ( $x_1 < 0.1$ ). Enthalpy of complex formation has been calculated both by thermochemical cycle and from the heats of mixing of equimolar amine-alcohol mixture in *n*-hexane. The values so obtained have been compared.

## 2. Experimental

### 2.1. Material

Methanol (Sarabhai), ethanol (B.D.H.), *n*-propanol (Reanal), and *n*-hexane (B.D.H.) were purified by the standard methods (Riddic and Bunger 1970). *n*-Butylamine (Fluka) was purified by fractional distillation over sodium hydroxide pellets, using one meter column packed with glass helices. All the compounds were dried over activated molecular sieve before use.

### 2.2. Heats of mixing

The heats of mixing of methanol and *n*-propanol with *n*-butyl amine have been determined at 30° C using a dewar type calorimeter with an accuracy of  $\pm 1\%$ . The details of the calorimeter and the procedure have been given in an earlier paper (Pradhan and Pathak 1980). The equimolar mixtures of *n*-butyl amine with methanol, ethanol and *n*-propanol were made by thorough mixing of exactly weighed quantities of compounds. The heats of mixing of these equimolar mixtures with *n*-hexane have been determined at 30° C.

## 3. Results and discussion

The heats of mixing of *n*-butyl amine with methanol and *n*-propanol are given in table 1 along with the values of  $\Delta H/x_1x_2$ . The partial molar enthalpy of mixing of *n*-butyl amine in methanol and propanol has been obtained by extrapolating the  $\Delta H/x_1x_2$  versus  $x_1$  curves to zero mole fraction of amine (figure 1). The enthalpies of butyl amine-methanol, ethanol and *n*-propanol complexes have been calculated by the thermochemical cycle using equation (1). The values of  $\Delta H_1$

Table 1. Heats of mixing of *n*-butylamine with methanol and *n*-propanol at 30° C.

Sl. No.	$x_1$ Mole fraction of butyl amine	$\Delta H$ J/mol	$\Delta H/x_1x_2$ kJ/mol
<b><i>CH<sub>3</sub>OH + n-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub></i></b>			
1.	0.0017	- 26.2	-15.43
2.	0.0034	- 50.8	-14.99
3.	0.0067	-100.2	-14.95
4.	0.0087	-128.1	-14.86
5.	0.0125	-180.2	-14.60
6.	0.0161	-222.4	-14.04
7.	0.0234	-312.4	-13.67
8.	0.0375	-454.7	-12.60
9.	0.0514	-591.1	-12.12
<b><i>n-C<sub>3</sub>H<sub>7</sub>OH + n-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub></i></b>			
1.	0.0013	- 14.7	-11.30
2.	0.0023	- 25.0	-10.87
3.	0.0046	- 49.4	-10.80
4.	0.0078	- 83.1	-10.60
5.	0.0120	-125.0	-10.36
6.	0.0173	-171.8	-10.10
7.	0.0225	-216.7	- 9.85
8.	0.0272	-250.8	- 9.48
9.	0.0378	-342.3	- 9.41

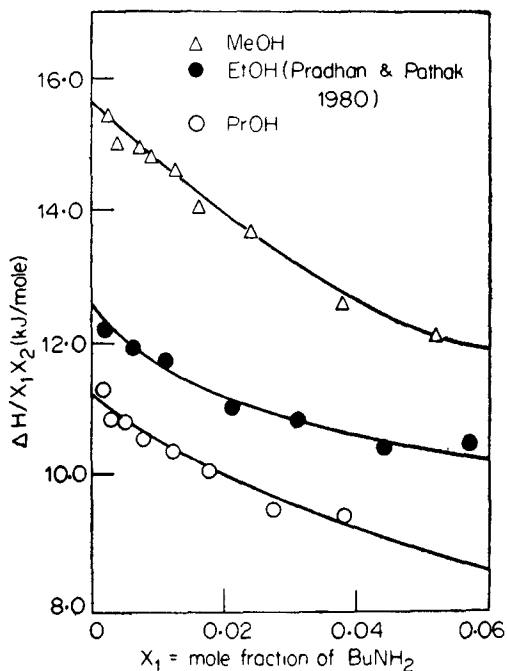


Figure 1.  $\Delta H/x_1x_2$  versus  $x_1$  curves for methanol, ethanol and *n*-propanol + *n*-butyl amine systems.

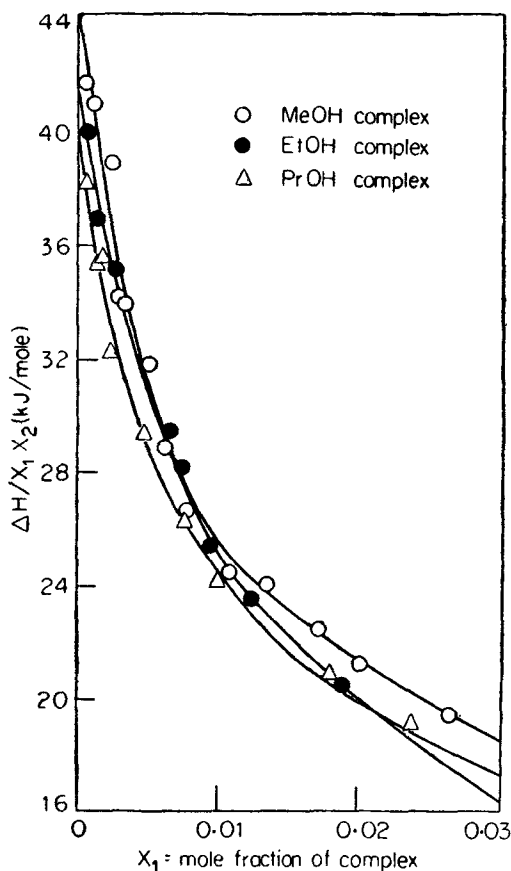


Figure 2.  $\Delta H/x_1x_2$  versus  $x_1$  curves for 1 : 1 molar mixtures of methanol, ethanol and *n*-propanol with butyl amine in *n*-hexane.

and  $\Delta H_4^\ddagger$  are taken from Duttachoudhury and Mathur (1976). The  $\Delta H_2$  value has been taken from Pradhan and Pathak (1980). The  $\Delta H_3$  values are obtained from figure 1. The ultimate enthalpies of complex formation are reported in table 3 along with the values obtained by Duttachoudhury and Mathur (1976) for ready comparison. It may be noted that the present values are higher by about 4 to 7 kJ/mole than those reported by Duttachoudhury and Mathur. This may be due to the lesser uncertainty involved in extrapolation in finding out the  $\Delta H_2$  and  $\Delta H_3$  values as in the present work the heats of mixing have been measured at very low mole fractions ( $x_1 = 0.001$ ).

The heats of mixing of equimolar mixture of *n*-butylamine-methanol, -ethanol and -propanol with *n*-hexane are given in table 2. The partial molar enthalpies of the mixtures in *n*-hexane have been obtained by extrapolating the  $\Delta H/x_1x_2$  versus  $x_1$  curve to zero mole fraction (figure 2). Here  $x_1$  represents the mole fraction of the mixture in *n*-hexane. The extrapolated values give directly the enthalpies of hydrogen bonded complex.

The enthalpies of hydrogen bonded complex are presented in table 3. It may be noted that the values obtained by this method are in excellent agreement with those obtained by the thermochemical cycle.

Table 2. Heats of mixing of amine-alcohol complexes with *n*-hexane at 30° C.

Sl. No.	$x_1$ mole fraction of complex	$\Delta H$ J/mole	$\Delta H/x_1x_2$ kJ/mol
<b><i>CH<sub>3</sub>OH-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub></i></b>			
1.	0.0005	20.9	41.80
2.	0.0011	45.2	41.13
3.	0.0024	93.1	38.89
4.	0.0028	196.0	34.38
5.	0.0032	108.3	33.94
6.	0.0050	158.1	31.78
7.	0.0061	176.4	29.10
8.	0.0078	205.6	26.57
9.	0.0107	258.8	24.45
10.	0.0133	315.5	24.04
11.	0.0172	380.8	22.53
12.	0.0200	417.0	21.28
13.	0.0264	500.0	19.46
<b><i>C<sub>2</sub>H<sub>5</sub>OH-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub></i></b>			
1.	0.0006	24.0	40.00
2.	0.0013	48.0	36.94
3.	0.0017	62.7	36.95
4.	0.0026	91.1	35.15
5.	0.0038	122.6	32.38
6.	0.0048	148.7	31.13
7.	0.0065	190.3	29.47
8.	0.0074	207.1	28.20
9.	0.0094	236.5	25.39
10.	0.0124	288.9	23.59
11.	0.0153	340.5	22.60
12.	0.0189	380.7	20.53
13.	0.0231	427.9	18.96
14.	0.0295	485.2	16.95
<b><i>C<sub>3</sub>H<sub>7</sub>OH-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub></i></b>			
1.	0.0005	19.1	38.20
2.	0.00125	44.2	35.40
3.	0.0017	60.5	35.65
4.	0.0025	80.3	32.20
5.	0.0046	134.6	29.40
6.	0.0077	202.5	26.51
7.	0.0100	238.7	24.11
8.	0.0182	375.4	21.01
9.	0.0239	445.2	19.09

Table 3. Enthalpy of *n*-butyl amine-alcohol complex.

Complex forming alcohol	By thermochemical cycle kJ/mol	By dissociation of complex kJ/mol	Literature* kJ/mol
Methanol	-44.3 ± 0.6	-44.0 ± 0.2	-37.5 ± 1.0
Ethanol	-40.8 ± 0.6	-41.0 ± 0.2	-35.4 ± 1.0
<i>n</i> -propanol	-39.4 ± 0.6	-39.5 ± 0.2	-35.0 ± 1.0

\* Duttachoudhury-Mathur (1976).

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