

## A simple calorimeter for the heats of mixing study of associated liquids : Enthalpy of hydrogen bonded ethanol-butylamine complex\*

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**Abstract.** A simple dewar type calorimeter has been constructed to determine the enthalpy of mixing in dilute concentration range and its performance checked by determining the heats of mixing of cyclohexane (1)-*n*-hexane (2) and ethanol (1) *n*-hexane (2) systems. The heats of mixing of *n*-butylamine with *n*-hexane and ethanol have been determined at 30°C. The enthalpy of ethanol-butylamine complex calculated by a thermochemical cycle was found to be  $-40.3$  kJ/mol.

**Keywords.** Calorimeter; ethanol-butylamine; heats of mixing; hydrogen bonding; thermodynamics.

### 1. Introduction

In our earlier work on the thermodynamic properties of binary mixtures of associated liquids (Duttachoudhury and Mathur 1976; Pradhan and Mathur 1978), the heats of mixing data below 0.05 mol fraction were not possible due to the intrinsic limitations of the twin-type calorimeter. Savini *et al* (1965) showed that in the case of associated liquids the heats of mixing data at the concentration as low as 0.01 mol fraction and below are necessary to get an accurate value of partial molar enthalpy of mixing or the enthalpy of hydrogen bonding. A simple calorimeter has, therefore, been constructed to determine more precisely the heats of mixing at a concentration as low as  $10^{-3}$  mol fraction. In the present paper the construction, the standardisation of the calorimeter and the results on the heats of mixing of *n*-butylamine with *n*-hexane and ethanol are reported.

### 2. Experimental

#### 2.1 Calorimeter

The calorimeter made of a double-walled corning glass vessel (160 ml capacity) with a side tube was mounted on a brass stand provided with four rods. It was then covered with a brass disc (lid) using a neoprene rubber O-ring fitted in the

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groove. The lid was tightly fixed by four nuts. The assembled calorimeter is shown in figure 1A. The lid has three openings for introducing a heating coil, a thermistor and a sample bulb. A teflon stirrer was fixed at the centre of the lid and a sample bulb was fixed inside the stirrer. The lid assembly is shown in figure 1B.

The component in smaller proportion was taken in a thin-walled glass bulb while the major component was taken in the calorimeter vessel. The weight of the sample in the bulb was in the range of 0.1 to 10 g while that of the major component was of 90 to 110 g. The calorimeter was immersed in a thermostat maintained at  $\pm 0.01^\circ\text{C}$  for about 3 hr to attain thermal equilibrium. The temperature of the thermostat was maintained by a Jumo mercury contact regulator. The temperature constancy was checked by a Beckmann thermometer (accuracy  $0.01^\circ\text{C}$ ). A Tempo bead-type thermistor (resistance  $33\text{ K}\Omega \pm 1\%$  at  $25^\circ\text{C}$ ) was used as the heat sensing element. The calorimeter heater was made of 36 SWG constantan wire (resistance  $80.20\text{ ohm}$ ). The resistance of the heating coil was measured by a digital-volt-ohm meter (accuracy  $0.01\text{ ohm}$ ). The heater and the thermistor leads were connected to the electrical circuit and wheatstone bridge respectively. The two arms of the wheatstone bridge were made of  $44.0 \pm 1\text{ k ohm}$  and  $11.5 \pm 0.1\text{ k ohm}$  carbon resistors. The third arm was made of  $11.0\text{ k ohm}$  halipot ten-turn resistor while the thermistor was connected in the fourth arm.

The imbalance in the wheatstone bridge due to change in the resistance of the thermistor was recorded on a Beckmann potentiometric recorder with three selecti-

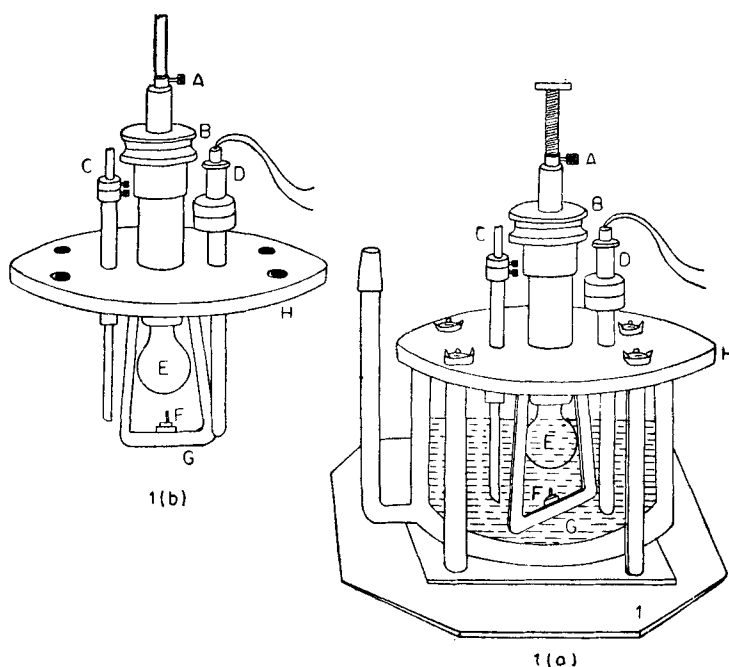


Figure 1. A schematic diagram of the calorimeter. A, bulb holding clamp; B, pulley; C, thermistor; D, heater; E, glass bulb; F, stainless steel wedge; G, teflon stirrer; H, calorimeter lid.

vities *viz.* 1, 10 and 100 mV. The liquids were constantly stirred using a synchronous motor of 300 r.p.m. The attainment of thermal equilibrium of the inside liquids was indicated by a steady base line on the recorder chart. The outer jacket of the calorimeter was then evacuated to a pressure of  $10^{-3}$  torr for 1 hr. The glass bulb was then pushed inside and broken by the stainless steel wedge at the centre of the stirrer. The temperature change due to mixing of the two liquids was recorded along with the heating or cooling curve due to heat leakage. The calorimeter was allowed to attain the thermostat temperature and calibration carried out by supplying a known amount of energy. The heating was adjusted as far as possible to the heat change obtained during the mixing process. The time for which current was passed was recorded on an electronic timer and the current was determined using a vernier potentiometer. The heat of mixing was then calculated as

$$\Delta H = \frac{i^2 R t}{(n_1 + n_2)} \times \frac{\Delta_1}{\Delta_2} \text{ joules/mole,}$$

where  $i$  is the current (in amp),  $t$  is the time in seconds,  $R$  is the resistance of the heater in ohms,  $\Delta_1$  and  $\Delta_2$  are the distances of separation between the initial and final traces of the recorder in the mixing and the calibration process respectively,  $n_1$  and  $n_2$  are the number of moles of the two liquids.

## 2.2 Errors in the measurement

In spite of the sufficient care to minimise the heat losses by evacuating the outer jacket of the calorimeter, there was a small heat leakage due to the vapour space (evaporation and condensation), and the heat exchange between the calorimeter and the surroundings. The vapour space which was minimised by filling the calorimeter almost completely varied between 15 and 30 ml depending on the quantity of the larger component. These errors were eliminated by calibration and measurement of the distances  $\Delta_1$  and  $\Delta_2$  on extrapolating the heating and cooling curves obtained at the end of mixing and calibration processes by the standard method (Skinner 1967). The contribution due to breaking of the bulb was negligible whereas the heat of stirring was 0.001 J/sec. The upper limits of errors in the measurements of various quantities were 0.05% in number of moles, 0.01% in current, 0.05% in resistance and 0.5% in  $\Delta_1$  and  $\Delta_2$  values. The overall probable error in heats of mixing value was of the order of  $\pm 1\%$ .

## 2.3 Materials

A.R. grade *n*-hexane (BDH) and cyclohexane (Pfizer) were purified by fractional distillation over  $P_2O_5$  whereas *n*-butylamine (Fluka) was fractionally distilled over sodium hydroxide. Constant boiling fractions were used for the experiments. Spectroscopic grade ethanol was used without further purification. All the compounds were dried over freshly activated molecular sieve before use.

## 3. Results and discussion

The performance of the calorimeter was checked by determining the heats of mixing of cyclohexane (1)-*n*-hexane (2) system throughout the concentration range

at 25° C. These values are given in table 1 along with the values calculated by the standard equation (Stokes-Marsh 1972)

$$\Delta H (\text{J/mole}) = x_1 (1 - x_1) [866 \cdot 1 - 249 \cdot 4 (1 - 2x_1) + 90 \cdot 7 (1 - 2x_1)^2 - 31 \cdot 8 (1 - 2x_1)^3]$$

The standard deviation in the present study was about 3 J/mol.

The performance of the calorimeter was further checked by studying the heats of mixing of ethanol (1)-*n*-hexane (2) system in the low concentration region (below 0.1 mol fraction of ethanol) at 30° C and the results are given in table 2. The plot of  $\Delta H/x_1x_2$  vs  $x_1$  is given in figure 2 along with the data obtained by Savini *et al* (1965) and both the values are in excellent agreement.

The heats of mixing of *n*-butylamine (1)-*n*-hexane (2) and *n*-butylamine (1)-ethanol (2) systems have been determined in the low concentration region ( $x_1 < 0.06$ ) at 30° C. The results are presented in table 2. The  $\Delta H/x_1x_2$  values are plotted as a function of  $x_1$  in figure 3. The *n*-butylamine-*n*-hexane system shows a strong endothermic behaviour which is due to the breaking of the hydrogen bonded associated species. The partial molar enthalpy of mixing obtained from the extrapolation of  $\Delta H/x_1x_2$  vs  $x_1$  curve to infinite dilution gives the enthalpy of  $\text{NH}_2 \cdots \text{NH}_2$  bond. The enthalpy of hydrogen bonded amino groups was 7.7 kJ/mol. The *n*-butylamine-ethanol system shows a strong exothermic behaviour. The negative heats of mixing is the result of two endothermic effects of dissociation of the associated amine and alcohol species by each other and the exothermic effect of hydrogen bonded complex formation between the amine and the alcohol molecules. Enthalpy of the hydrogen bonded complex ( $\Delta H_5$ ) has been calculated by a thermochemical cycle (Murakami and Fujishiro 1966) as

$$\Delta H_5 = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4, \quad (2)$$

where  $\Delta H_1$  and  $\Delta H_2$  are the enthalpies of hydrogen bonding of ethanol and *n*-butylamine respectively.  $\Delta H_3$  is the partial molar enthalpy of *n*-butylamine in

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

Mole fraction of cyclohexane ( $x_1$ )	$\Delta H$ J/mol	$\Delta H$ J/mol calculated by equation
0.0826	50.5	53.6
0.1441	87.3	89.5
0.2079	120.4	123.4
0.2412	140.6	138.8
0.4781	215.3	213.4
0.6430	212.1	217.2
0.7818	178.4	177.9
0.9183	83.3	87.1

Standard deviation : 2.96 J/mol.

Table 2. Heats of mixing of ethanol-*n*-hexane, *n*-butylamine-*n*-hexane and *n*-butylamine-ethanol systems at 30° C.

$x_1$	$\Delta H$ J/mol	$\Delta H/x_1x_2$ kJ/mol
<i>Ethanol</i> (1) + <i>n</i> - <i>hexane</i> (2)		
0.0062	122.3	19.85
0.0132	226.2	17.63
0.0184	259.7	14.38
0.0221	292.4	13.53
0.0338	354.7	10.86
0.0397	356.8	9.36
0.0508	377.3	7.83
0.0637	409.6	6.87
0.1208	521.4	4.91
<i>n</i> - <i>Butylamine</i> (1) + <i>n</i> - <i>hexane</i> (2)		
0.0014	10.4	7.44
0.0038	26.9	7.11
0.0072	48.0	6.71
0.0120	73.6	6.20
0.0155	90.3	5.92
0.0163	95.2	5.94
0.0198	112.3	5.79
0.0215	117.2	5.57
0.0253	143.7	5.83
0.0325	169.5	5.39
0.0344	182.0	5.48
0.0485	242.8	5.26
<i>n</i> - <i>Butylamine</i> (1) + <i>ethanol</i> (2)		
0.00125	-15.2	-12.18
0.0059	-70.1	-11.95
0.0108	-125.8	-11.77
0.0156	-173.7	-11.31
0.0211	-229.0	-11.04
0.0308	-324.8	-10.88
0.0438	-438.6	-10.47
0.0569	-562.9	-10.49

ethanol medium and  $\Delta H_4$  is the dipolar stabilisation energy of ethanol-*n*-butylamine complex (Duttachoudhury and Mathur 1976). The  $\Delta H_1$  and  $\Delta H_2$  values were obtained by extrapolating the  $\Delta H/x_1x_2$  vs  $x_1$  curves to zero mole fraction of alcohol and amine in *n*-hexane while  $\Delta H_3$  value was obtained by extrapolating the curve for *n*-butylamine-ethanol to zero mole fraction of butylamine. The  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  values were +23.6, +7.7, -12.3 kJ/mol respectively. The value of dipolar stabilisation enthalpy of butylamine-ethanol complex ( $\Delta H_4$ ) was taken as 3.27 kJ/mol (Duttachoudhury and Mathur 1976). The ultimate

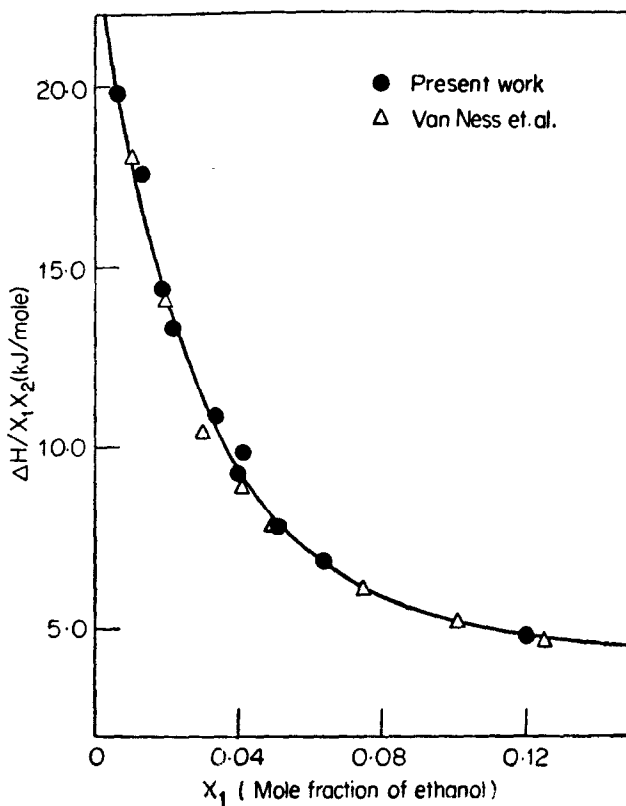


Figure 2.  $\Delta H/x_1x_2$  versus  $x_1$  curve for ethanol (1)-*n*-hexane (2) system.

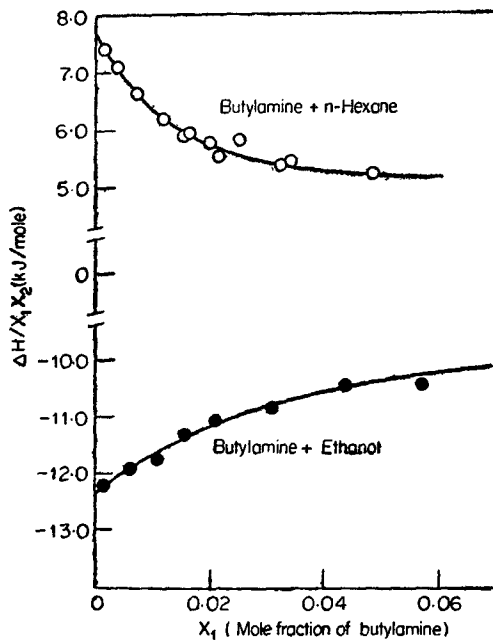


Figure 3.  $\Delta H/x_1x_2$  versus  $x_1$  curves for *n*-butylamine (1)-*n*-hexane (2) and *n*-butylamine (1)-ethanol (2) systems.

enthalpy of complex formation ( $\Delta H_5$ ) obtained by equation (2) was found to be  $-40.3 \pm 0.6$  kJ/mol and appears to be quite reliable as the uncertainties in the extrapolation of the  $\Delta H/x_1x_2$  vs  $x_1$  curves to zero mole fraction have been minimised by obtaining the  $\Delta H$  values at much lower mole fractions. This value is higher than that reported by Duttachoudhury and Mathur (1976), viz., 35.5 kJ/mol.

### **Acknowledgement**

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