

Heats of Mixing of *n*-Butyl Amine–Water and *n*-Butyl Amine–Alcohol Systems

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The heats of mixing for binary mixtures of *n*-butyl amine with water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and *n*-butyl alcohol at $40.00 \pm 0.01^\circ\text{C}$ determined in a twin-type calorimeter can be fitted in an equation of the form $\Delta H^m = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2]$ where x_2 is the mole fraction of *n*-butyl amine; x_1 is the mole fraction of the second component; B , C , and D are constants. The mixing is accompanied by evolution of heat, and the exothermic effect follows the order $\text{CH}_3\text{OH} > \text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > n\text{-C}_3\text{H}_7\text{OH} > n\text{-C}_4\text{H}_9\text{OH}$.

As part of our program of research to investigate the effect of a gradual change in the size and shape of the substituent hydrocarbon group on the thermodynamic properties of a mixture of highly polar liquids, we present the results of studies on the heats of mixing of *n*-butyl amine with water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and *n*-butyl alcohol.

Experimental

The heat of mixing experiments were conducted at 40°C in a twin calorimeter system, similar to the one described by Adcock and McGlashan (1), with minor modifications. The mixing vessels were made of stainless steel with a suitable insulation to prevent the conduction of heat out of the calorimeter. Because of the reactive nature of the *n*-butyl amine, the heater wires were enclosed in a 20-SWG teflon sleeving. One of the liquids was enclosed in a glass tube with a thin glass membrane blown at one end which was punctured at the time of mixing by the sharp stainless-steel point in the upper part of the mixing vessel. The temperature-sensitive elements were a matched pair of thermistors with their resistances matched to within 1% and were obtained from M/s Tempo Semiconductors, Bombay. The matching of the resistances was confirmed by the measurement of their resistances at 25° , 35° , and 45°C . The temperature of the thermostat bath was controlled at 40°C to within $\pm 0.01^\circ\text{C}$.

n-Butyl amine (supplied by Riedel, Germany) was kept over sodium hydroxide pellets for several days and then fractionally distilled. The middle fraction, whose boiling temperature was 74.6°C at 708 torr, was separated for use and kept over a 3A Linde molecular sieve for dehydration. The density at 25°C of the purified *n*-butyl amine was measured as 0.73310, a value which is in good agreement with 0.73308 reported by Letcher (8). Analar-grade alcohols were refluxed with alkaline silver nitrate and then fractionally distilled. The middle fractions, boiling at constant temperatures, were separated for use and dehydrated over a 3A Linde molecular sieve. The densities of the alcohols determined by us along with the values reported in the literature are summarized in Table I.

The purity of the materials used was also confirmed by glc analysis with a SE-30 column, where only a single sharp peak was obtained in each case. Water used for the heat of mixing experiments was obtained by redistill-

ing distilled water in an alkaline permanganate medium. The performance of the twin calorimeter system and the accuracy of the results obtained were checked by comparing the results of the experiments on the heat of mixing of the methyl alcohol–water system at 25°C with the results already available in the literature (3, 7).

The choice of the exothermic reaction rather than an endothermic reaction as chosen by others (9, 10) was dictated by the fact that the results of the former directly reflect any changes in the matching of the thermistors or any imbalance in the heat capacities of the two parts, viz., the mixing vessel and the compensating vessel of the calorimeter. In an endothermic reaction, the heat compensation is carried in the mixing vessel itself; hence, any difference in the heat capacities of the calorimeter vessels or the mismatching of the thermistor resistances in the twin calorimeter system will not be detected in the results of the heat of mixing.

Recently, Akhlaq (2) recommended that the *n*-hexane–cyclohexane system should be treated as an international standard for checking the performance of a mixing calorimeter system designed for the determination of the heats of mixing of liquids. In view of the difficulties pointed out earlier, it will not be advisable to use the results of the heats of mixing of an endothermic system such as *n*-hexane–cyclohexane for checking the performance of a calorimetric system if it is to be used for exothermic reactions.

The results obtained by us on the heats of mixing of the $\text{CH}_3\text{OH}\text{--H}_2\text{O}$ system at 25°C summarized in Table II are in good agreement with those obtained by Lama and Benjamin (7) and Benjamin and Benson (3) as shown in Figure 1.

Table I. Densities of Pure Liquids at 25°C

	This work	Lit	Ref
<i>n</i> -Butyl alcohol	0.80580	0.80583	11
<i>n</i> -Propyl alcohol	0.79955	0.79950	6
Ethyl alcohol	0.78503	0.78508	4
Methyl alcohol	0.78673	0.78675	5

Table II. Heat of Mixing of $\text{CH}_3\text{OH}\text{--H}_2\text{O}$ System at 25°C

$x_1 =$ mole fraction of CH_3OH in mixture	$\Delta H^m, \text{J mol}^{-1}$
0.0376	−239.7
0.0535	−332.2
0.1002	−569.8
0.1284	−667.0
0.1677	−745.5
0.1765	−779.3
0.2277	−865.1
0.3130	−876.8
0.3438	−868.6
0.4809	−809.4
0.7220	−594.9
0.7685	−527.1
0.8725	−304.5

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Table III. Heats of Mixing at 40°C of H₂O-*n*-C₄H₉NH₂, CH₃OH-*n*-C₄H₉NH₂, C₂H₅OH-*n*-C₄H₉NH₂, *n*-C₃H₇OH-*n*-C₄H₉NH₂, and *n*-C₄H₉OH-*n*-C₄H₉NH₂ Systems as Function of Mole Fraction of First Component

System	x_1	ΔH^m , kJ mol ⁻¹	$\Delta H^m/x_1x_2$, kJ mol ⁻¹	System	x_1	ΔH^m , kJ mol ⁻¹	$\Delta H^m/x_1x_2$, kJ mol ⁻¹
Water- <i>n</i> -butyl amine	0.3039	-2.4375	-11.523	Ethanol- <i>n</i> -butyl amine	0.7862	-2.0852	-12.405
	0.3719	-2.9131	-12.471		0.9049	-1.1028	-12.814
	0.3771	-3.0042	-12.789	1-Propanol- <i>n</i> -butyl amine	0.1344	-1.1602	-9.976
	0.4484	-3.1368	-12.682		0.1740	-1.3939	-9.700
	0.4511	-3.1855	-12.865		0.2484	-1.9108	-10.234
	0.5200	-3.3702	-13.502		0.3518	-2.5382	-11.132
	0.5390	-3.4986	-14.080		0.4422	-2.7966	-11.336
	0.5957	-3.3683	-13.987		0.5146	-2.9029	-11.621
	0.6682	-3.0288	-13.661		0.5673	-2.7423	-11.170
	0.7239	-2.7394	-13.706		0.6251	-2.7016	-11.531
	0.8075	-2.3260	-14.964		0.6957	-2.4707	-11.671
	0.8352	-1.9275	-14.004		0.7914	-1.8685	-11.317
	0.8379	-1.8611	-13.703	0.8594	-1.4104	-11.675	
	0.9243	-0.9272	-13.251	0.9154	-0.9634	-12.447	
Methyl alcohol- <i>n</i> -butyl amine	0.1842	-1.7713	-11.785	1-Butyl alcohol- <i>n</i> -butyl amine	0.0728	-0.6253	-9.264
	0.2853	-2.7102	-13.292		0.1031	-0.8780	-9.495
	0.4277	-3.4932	-14.270		0.1246	-1.1034	-10.116
	0.5387	-3.7131	-14.942		0.1896	-1.5496	-10.085
	0.6409	-3.6412	-15.821		0.2694	-2.0151	-10.254
	0.7094	-3.3604	-16.297		0.2774	-1.9446	-9.701
	0.7159	-3.3190	-16.318		0.3207	-2.1672	-9.948
	0.7732	-2.9258	-16.676		0.3871	-2.4200	-10.200
	0.8111	-2.4473	-16.301		0.3907	-2.4779	-10.409
	0.9130	-1.2605	-15.875		0.4264	-2.6814	-10.963
Ethanol- <i>n</i> -butyl amine	0.1375	-1.1588	-9.771		0.4847	-2.7878	-11.161
	0.2984	-2.2133	-10.570		0.5005	-2.7326	-10.993
	0.3665	-2.5807	-11.114		0.5480	-2.8021	-11.312
	0.3980	-2.6368	-11.005		0.5756	-2.7785	-11.374
	0.4778	-2.8065	-11.248	0.6370	-2.5852	-11.180	
	0.5106	-2.9170	-11.673	0.7191	-2.4126	-11.944	
	0.5552	-2.8881	-11.693	0.7238	-2.1207	-10.609	
	0.6216	-2.8753	-12.225	0.7718	-1.9741	-11.209	
	0.6762	-2.6820	-12.247	0.8591	-1.4642	-12.096	
	0.7422	-2.4007	-12.549	0.9178	-0.7685	-10.187	

Table IV. Values of Constants in Equation 1

System	B, kJ mol ⁻¹	C, kJ mol ⁻¹	D, kJ mol ⁻¹
Water- <i>n</i> -butyl amine	-13.342	-2.611	+2.546
Methyl alcohol- <i>n</i> -butyl amine	-15.164	-3.570	+2.698
Ethyl alcohol- <i>n</i> -butyl amine	-11.536	-1.891	+0.427
1-Propyl alcohol- <i>n</i> -butyl amine	-11.329	-1.200	+1.406
1-Butyl alcohol- <i>n</i> -butyl amine	-10.952	-1.372	+0.935

Table V. Values of $\Delta H^m/x_1x_2$ at $x_1 = 0$ and $\Delta H^m/x_1x_2$ at $x_2 = 0$

System	$\Delta H^m/x_1x_2$ at $x_1 = 0$, kJ mol ⁻¹	$\Delta H^m/x_1x_2$ at $x_2 = 0$, kJ mol ⁻¹
Water- <i>n</i> -butyl amine	-8.1	-13.5
Methyl alcohol- <i>n</i> -butyl amine	-9.0	-15.9
Ethyl alcohol- <i>n</i> -butyl amine	-9.2	-13.0
1-Propyl alcohol- <i>n</i> -butyl amine	-8.8	-11.1
1-Butyl alcohol- <i>n</i> -butyl amine	-8.6	-11.4

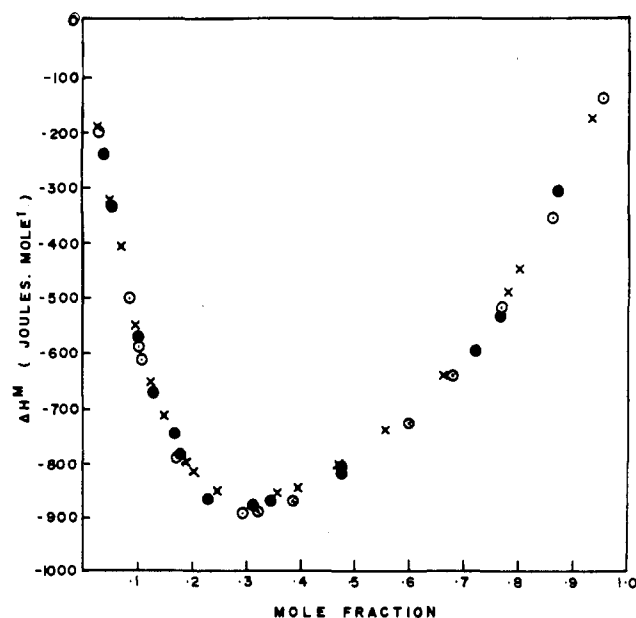


Figure 1. Heats of mixing of methyl alcohol-water system at 25°C in J mol of mixture as function of mole fraction of methyl alcohol obtained in twin calorimeter system

● Present work
× (7)
○ (3)

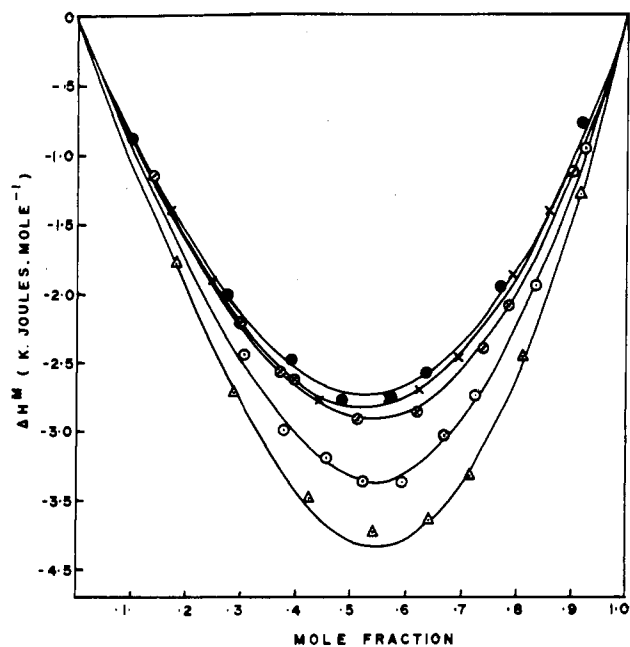


Figure 2. Heats of mixing at 40°C in kJ mol⁻¹ of binary mixture as function of mole fraction of first component

Curve I ○ Water-*n*-butyl amine
 Curve II △ Methanol-*n*-butyl amine
 Curve III ⊙ Ethanol-*n*-butyl amine
 Curve IV × 1-Propanol-*n*-butyl amine
 Curve V ● 1-Butanol-*n*-butyl amine

Results and Discussions

The measurements of the heat of mixing were carried out on binary mixtures of *n*-butyl amine with water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and *n*-butyl alcohol at 40° ± 0.01°C. The results obtained are summarized in Table III where x_1 is the mole fraction of the component first named, ΔH^m is the heat of mixing expressed in kJ mol⁻¹ of the mixture, and x_2 is the mole fraction of component 2. The plots of the ΔH^m as the function of x_1 are shown in Figure 2. The results summarized in Table III have been fitted by the method of least squares in an equation of the form:

$$\Delta H^m = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2] \quad (1)$$

The values of the constants B , C , and D in the equations are tabulated in Table IV.

The values of $\Delta H^m/x_1 x_2$, given in Table V, have been plotted as a function of x_1 in Figure 3. The values of $\Delta H^m/x_1 x_2$ at $x_1 = 0$ correspond to the energy changes associated with the transfer of 1 mole from the pure water/alcohol state to that in which each water/alcohol molecule makes a hydrogen bond with an *n*-butyl amine molecule and in which such water/alcohol-*n*-butyl amine complexes are surrounded with a large number of *n*-butyl amine molecules. Similarly, the values of $\Delta H^m/x_1 x_2$ at $x_2 = 0$ correspond to the energy changes associated with the transfer of 1 mole from the pure *n*-butyl amine state

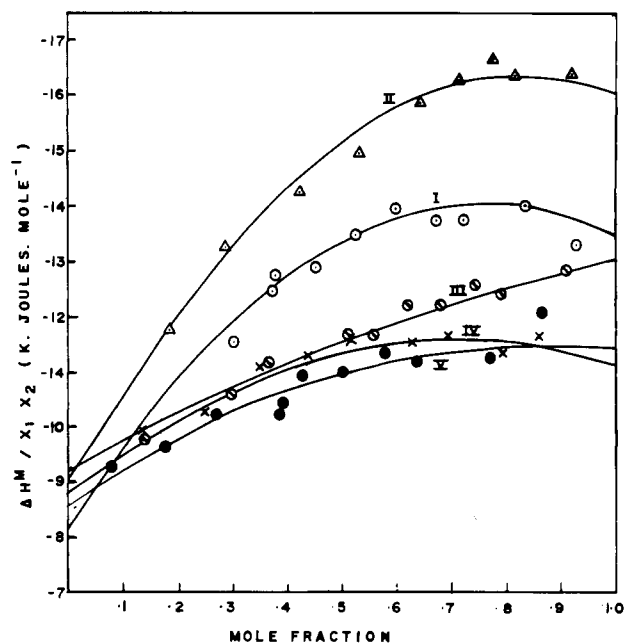
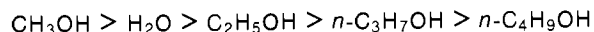


Figure 3. Plots of $\Delta H^m/x_1 x_2$ values at 40°C in kJ mol vs. mole fraction of first component

Curve I ○ Water-*n*-butyl amine
 Curve II △ Methanol-*n*-butyl amine
 Curve III ⊙ Ethanol-*n*-butyl amine
 Curve IV × 1-Propanol-*n*-butyl amine
 Curve V ● 1-Butanol-*n*-butyl amine

to that in which each *n*-butyl amine molecule makes a hydrogen bond with a water/alcohol molecule and in which such *n*-butyl amine-water/alcohol complexes are surrounded with a large number of water/alcohol molecules.

The curves shown in Figure 2 are slightly asymmetric, each having a minimum in the region of mole fraction 0.5 to 0.6. The order of the heats of mixing of *n*-butyl amine-alcohol/water systems may be expressed as:



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