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Excess Free Energy of Binary Mixtures of *n*-Butylamine with Ethyl Alcohol & *n*-Propyl Alcohol*

M. K. DUTTA CHOUDHURY
National Chemical Laboratory, Poona 8

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The excess free energy of mixing G^E has been calculated from the isothermal vapour liquid equilibrium data of *n*-butylamine+ethanol and *n*-butylamine+1-propanol binary mixtures at 40°C. A recirculating equilibrium still has been used for the measurement of the vapour liquid equilibria of the binary mixtures at constant temperature. The values of G^E at 40°C have been used with our previously reported values of H^E to get the values of TS^E. The values of H^E, TS^E and G^E thus obtained are found to be highly negative for all the systems throughout the concentration ranges indicating a specific interaction between *n*-butylamine and *n*-alcohols.

IN continuation of our earlier work[1] on heats of mixing of *n*-butylamine with water and some normal aliphatic alcohols we present here the results of our studies on the excess free energy of mixing of *n*-butylamine with ethanol and 1-propanol.

Materials and Methods

The chemicals used in the present investigation and the method of their purification and the checking of purity have been given in an earlier communication[1].

A modified Jones-Colburn recirculating still[2] was chosen for the determination of the vapour liquid equilibria since it was possible to obtain a thermal equilibrium in 30 min as well as conduct experiments with a small quantity (20 ml) of the liquid mixture. The system pressure in the circulating still was adjusted to a desired value by connecting the still to the vacuum system via manometer and a micrometer needle regulating valve. The equilibrium pressure was determined from the difference of the barometer reading and the manometer reading after appropriate corrections for expansion of mercury and for the difference in the room temperature and the temperature of calibration of the cathetometer used for reading the manometer. A value of '*g*' equal to 978·59 cm/sec^2 valid for Poona was used in the calculation of the pressure.

The composition of the binary liquid mixtures of *n*-butyl amine with alcohols was determined either (i) by a potentiometric titration of the *n*-butyl amine in a weighed quantity of the mixture dissolved in water with a standardized hydrochloric acid solution or (ii) by the previously determined relation between the density of a liquid mixture at 25° and its composition. Both the methods gave results in agreement with one another except that the potentiometric titration method gave results tended to be inaccurate for the composition of the binary mixtures with very large amine/alcohol ratios possibly due to the increased loss of the amine by evaporation during weighing, transfer and titration of the mixture. In such cases compositions were determined by the density method.

The liquid phase activity coefficients γ_1 and γ_2 were calculated by the equations:

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 p_1} + \frac{(B_{11}-V_1^L)(P-p_1)}{RT} + \frac{P\delta_{12} y_2^2}{RT} \quad \ldots(1)$$

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 p_2} + \frac{(B_{22}-V_2^L)(P-p_2)}{RT} + \frac{P\delta_{12} y_1^2}{RT} \quad \ldots(2)$$

where p_1 and p_2 are the vapour pressures, x_1 and x_2 are the mole fractions in liquid phase, y_1 and y_2 are the mole fractions in the vapour phase, V_1^L and V_2^L are molar liquid volumes of the components (1) and (2) respectively. P is the system equilibrium pressure, B_{11} and B_{22} are the second virial coefficients of the pure components (1) and (2) respectively and

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad \ldots(3)$$

where B_{12} is the second virial cross coefficient of the mixture and given by the expression:

$$B_{12} = (B - y_1^2 B_{11} - y_2^2 B_{22})/2y_1 y_2 \quad \ldots(4)$$

where B is the second virial coefficient of the mixture.

The experimental values of the second virial coefficients for most of the components are not available in the literature, although the values of the second virial coefficient for pure ethanol have been reported by several groups of workers[3-5]. The values, extrapolated at 40° however, show wide variations (Table 1). The values of the second virial coefficient for pure 1-propanol have been reported by Cox[6] for temperature interval 105-150°. He has also given an expression for calculating the value of the virial coefficient of 1-propanol as a function of temperature. The values of the second virial coefficients for ethanol, 1-propanol and *n*-butylamine used by us for the calculation of the activity coefficients were those determined from Pitzer-Curl[7] equation. The effect of the second virial coefficients on excess free energy of mixing is small particularly at low pressure. Any error arising out of the differences in the actual values

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*NCL communication No. 1958.

TABLE 1 — VALUES OF THE SECOND VIRIAL COEFFICIENTS AT DIFFERENT TEMPERATURES

Substance	Temp. (°C)	Values of second virial coefficients				
		Ref. 3	Ref. 4	Ref. 5	Present calculation	Ref. 6
Ethanol	40	−2134	−2500*	−3800	−1136	—
	60	−1285	−1522	−1990	—	—
	80	−938	−941	−1330	—	—
1-Propanol	40	—	—	—	−1665	−1808*
	115	—	—	—	—	−913
	120	—	—	—	—	−781
	135	—	—	—	—	−619
	150	—	—	—	—	−606
n-Butylamine	40	—	—	—	−1496	—

*Extrapolated values.

of the second virial coefficients and those calculated by the Pitzer-Curl equation may therefore be neglected. The calculated values of the second virial coefficients are given in Table 1, along with the data already available. Following the method of Boublikova and Lu[8], the values of B_{12} have been taken to be equal to $(B_{11} \times B_{22})^{\frac{1}{2}}$. The values of the molar volumes V^L at 40° for ethanol, 1-propanol and *n*-butylamine are 59·6, 76·0 and 102·0 millilitres respectively.

The thermodynamic test for the internal consistency of the experimental data were performed by Herington's[9] method according to which

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = 0$$

which means that the algebraic area bound by $x_1 = 0$ and $x_1 = 1$ in the plot of log γ_1/γ_2 versus x_1 should be zero.

The performance of the modified Jones-Colburn still used by us was checked by an actual vapour liquid equilibrium experiment with ethanol+water system at 50°, comparing the results with those available in the literature[10,11] and subjecting these results to the thermodynamic consistency test. The vapour liquid equilibrium data of ethanol and water system at 50° obtained are given in Table 2. The plots of log γ_1/γ_2 versus x_1 are shown in Fig. 1. Our data showed a deviation of 1·4% compared to 4·8% for the data of Dulitskaya[10] and 23% for the data of Udovenko[11].

Results and Discussion

The results of the vapour liquid equilibrium studies at 40° for *n*-butylamine+ethanol and *n*-butylamine+1-propanol systems are given in Table 3. The values of the excess Gibb's free energy G^E were determined from the relation

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

The *P-x,y* diagram for the system *n*-butylamine+ethanol is shown in Fig. 2 as typical of the two systems studied. The presence of azeotropes at 0·32 mole fraction of *n*-butylamine for *n*-butylamine+ethanol and at 0·09 mole fraction of *n*-butylamine for *n*-butylamine+1-propanol systems have been observed. The azeotrope formation is more clearly understood from the *x-y* plot for *n*-butylamine-ethanol system (inset in Fig. 2) is typical of the two systems. The plots of log γ_1/γ_2 versus x_1 for both the

TABLE 2 — VAPOUR LIQUID EQUILIBRIUM DATA FOR ETHANOL (1) + WATER (2) BINARY MIXTURE AT 50°

[x_1 = mole fraction of component (1) in liquid; y_1 = mole fraction of component (1) in vapour; and P = total solution vapour pressure]

x_1	y_1	P (mm of Hg)	log γ_1/γ_2
0 0000	0·0000	92·51	—
0·0267	0·2371	108·66	0·6767
0·0743	0·4127	138·34	0·5649
0·1333	0·5225	170·22	0·4746
0·2174	0·5817	187·71	0·3218
0·2795	0·6096	192·64	0·2274
0·3673	0·6332	199·98	0·0941
0·4317	0·6500	202·48	0·0106
0·5660	0·7000	200·72	−0·1247
0·6641	0·7394	215·49	−0·2206
0·7802	0·8064	211·44	−0·3080
0·8308	0·8454	222·87	−0·3308
0·9070	0·9070	225·41	−0·3775
1·000	1·000	220·6	—

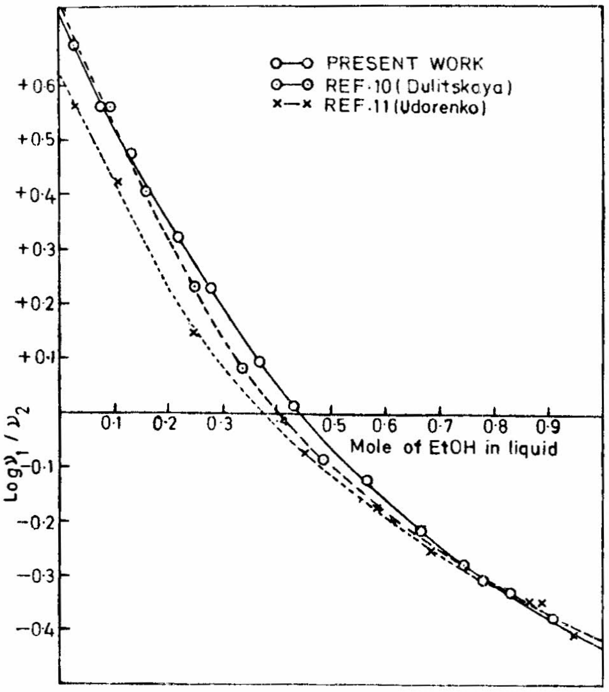

Fig. 1 — Thermodynamic consistency test for ethanol (1)-water (2) system at 50° [(○—○) Present work (deviation = 1·4%); (○—○) ref. 10 (deviation = 4·8%); and (×—×) ref. 11 (deviation = 23%)]

systems shown in Fig. 3 indicated a deviation of $<2\%$ for *n*-butylamine+ethanol and $<3\%$ for *n*-butylamine+1-propanol systems.

The values of G^E are negative throughout the concentration ranges and the minimum values of G^E are found to be -885 J mole^{-1} at 0·46 mole fraction of *n*-butylamine for the *n*-butylamine+ethanol system and -710 J mole^{-1} at 0·44 mole fraction of the amine for *n*-butylamine+1-propanol

TABLE 3 — VAPOUR-LIQUID EQUILIBRIUM OF *n*-BUTYLAMINE (1)+ETHANOL (2) AND *n*-BUTYLAMINE (1)+1-PROPANOL (2) SYSTEMS AT 40°

Mole fraction of *n*-butylamine in liquid x_1	Mole fraction of *n*-butylamine in vapour y_1	P in mm	$\log \gamma_1$	$\log \gamma_2$	G^E (J mole^{-1})
n-BUTYLAMINE (1)-ETHANOL (2) SYSTEM					
0·1202	0·0708	123·24	−0·4093	−0·0123	−355·19
0·2037	0·1603	118·30	−0·3011	−0·0307	−507·63
0·2939	0·2838	115·53	−0·2226	−0·0577	−628·23
0·3835	0·4263	115·99	−0·1598	−0·0933	−703·04
0·4409	0·5224	119·45	−0·1195	−0·1177	−701·26
0·5355	0·6641	128·47	−0·0685	−0·1586	−653·03
0·6020	0·7451	136·66	−0·0429	−0·1847	−587·88
0·6970	0·8422	146·56	−0·0233	−0·2441	−535·21
0·8214	0·9312	162·60	−0·0065	−0·3302	−380·58
0·8864	0·9640	172·19	−0·0001	−0·3901	−262·81
1·0000	1·0000	187·50*	0·0000	0·0000	0·00
0·0000	0·0000	134·00†	0·0000	0·0000	0·00
n-BUTYLAMINE (1)-1-PROPANOL (2) SYSTEM					
0·0404	0·0383	52·37	−0·5723	−0·0051	−167·95
0·1139	0·1304	52·50	−0·4894	−0·0131	−403·84
0·2329	0·3474	56·29	−0·3444	−0·0450	−687·94
0·2766	0·4367	60·11	−0·2913	−0·0551	−720·32
0·3880	0·6426	70·59	−0·2010	−0·1104	−872·75
0·4900	0·7850	87·09	−0·1247	−0·1615	−860·27
0·5890	0·8785	105·41	−0·0736	−0·2335	−839·35
0·6897	0·9315	124·40	−0·0455	−0·2892	−726·26
0·7300	0·9510	133·77	−0·0299	−0·3430	−686·21
0·7842	0·9682	145·20	−0·0180	−0·3984	−600·34
0·8494	0·9818	158·27	−0·0083	−0·4474	−446·30
0·8811	0·9870	164·15	−0·0073	−0·4757	−377·70
1·0000	1·0000	187·50*	0·0000	—	000·00
0·0000	0·0000	53·1‡	—	—	—

*Pure *n*-butylamine.
†Pure ethanol.
‡Pure 1-propanol.

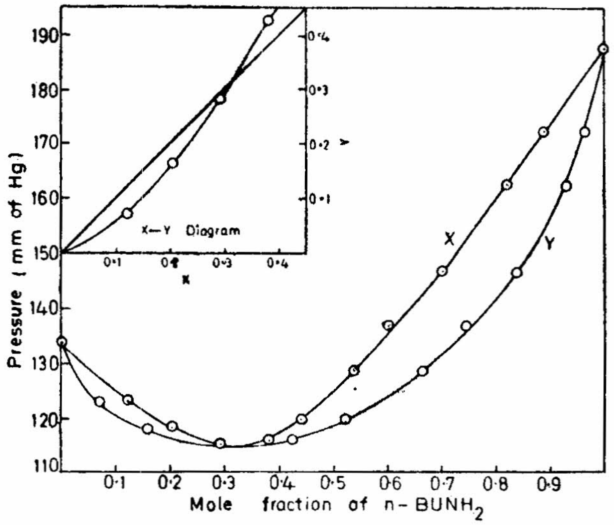

Fig. 2 — P-x,y diagram for n-BuNH$_2$(1) + ethanol (2) system at 40° [Azeotrope formation is at 0·32 mole fraction of *n*-butylamine, shown in the *x-y* diagram (inset)]

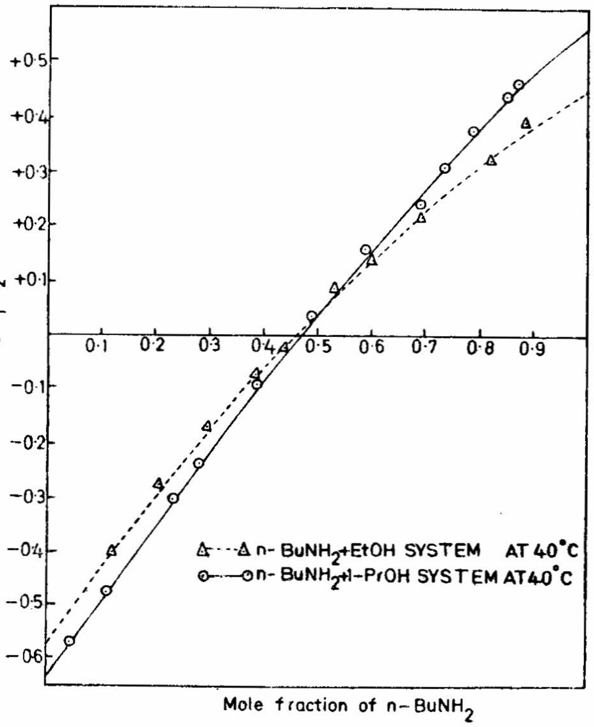

Fig. 3 — Thermodynamic consistency test for n-BuNH$_2$ (1) + ethanol (2) system at 40° [Δ—Δ (deviation $<2\%$); and for n-BuNH$_2$ (1) + 1-propanol (2) system at 40°, (⊙—⊙) (deviation $<3\%$)]

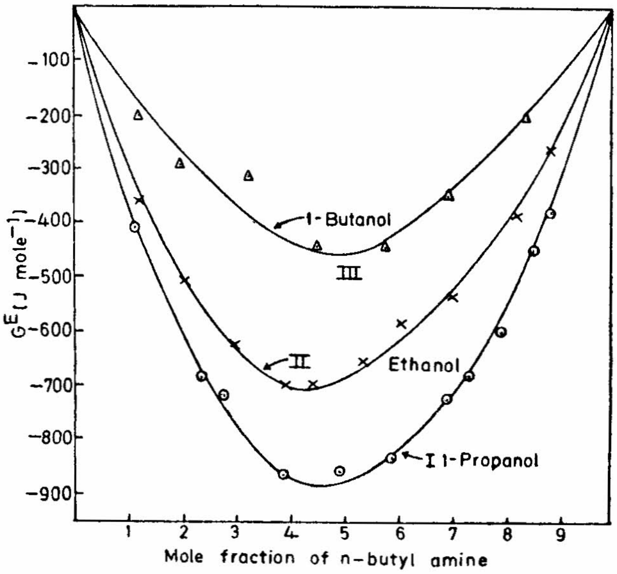

Fig. 4 — Excess free energy of mixing at 40° as a function of the mole fraction (x_1) of n-BuNH$_2$ for (1) n-BuNH$_2$ (1)-1-propanol(2), (ii) n-BuNH$_2$ (1)-ethanol, and (iii) n-BuNH$_2$ (1)-1-butanol (2) systems

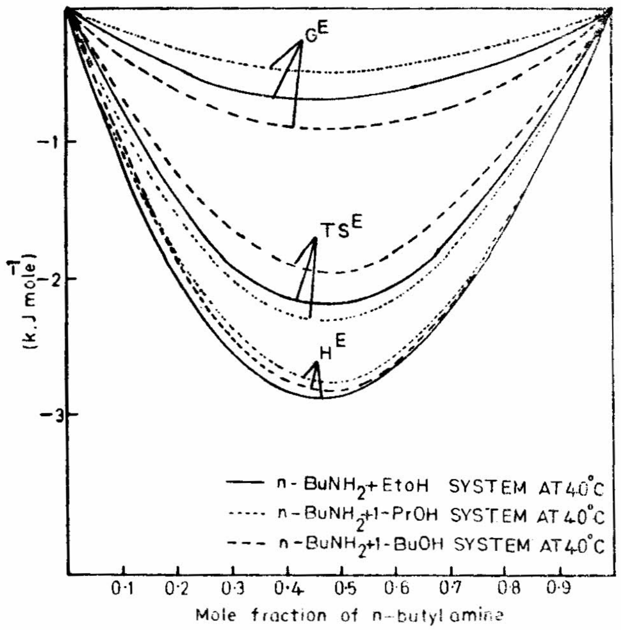

Fig. 5 — Values of thermodynamic function H^E, G^E and TS^E as a function of mole fraction (x_1) of *n*-butylamine for binary mixtures of *n*-butylamine with (1) ethanol, (2) 1-propanol and (3) 1-butanol

system. Fig. 4 shows the plots of G^E versus the mole fraction x_1 of *n*-butylamine in the liquid phase.

Ratkovics *et al.*[12] reported the values of the excess free energy of mixing of *n*-butylamine+1-butanol system at 40° but did not report the presence of any azeotrope for this system. The values of G^E for *n*-butylamine+1-butanol system at 40° obtained by Ratkovics *et al.* have also been plotted in Fig. 4 along with our results on the *n*-butylamine+ethanol and *n*-butylamine+1-propanol systems. Although Ratkovics' data show some scattering, a smooth curve drawn through the experimental points has the shape of a parabola with minimum value of G^E equal to -455 J mole^{-1} at *n*-butylamine mole fraction of 0·48.

It may be observed that the value of G^E and the values of H^E reported earlier[1] for the binary mixtures of *n*-butylamine with ethanol, 1-propanol and 1-butanol are negative throughout the concentration ranges and fall on a nearly symmetrical parabolic curve in plots of G^E and/or H^E versus mole fraction of *n*-butylamine. The values of TS^E at 40°C, obtained from the relation $TS^E = H^E - G^E$, are also found to be negative and when plotted versus x_1 also give symmetrical parabolic curves with minima close to 0·5 mole fraction of *n*-butylamine (Fig. 5). The thermodynamic excess properties for the binary mixtures of *n*-butylamine with ethanol, 1-propanol and 1-butanol follow the order

$$-H^E > -TS^E > -G^E \text{ and } G^E < 0$$

The high negative values of the thermodynamic excess functions indicate a strong specific interaction between *n*-butylamine and ethanol, 1-propanol or 1-butanol, leading to specific chemical species in solution.

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