

## Acknowledgment

The authors acknowledge the assistance of P. Belanger for the X-ray diffraction identification of the jarosite-type compounds.

## Literature Cited

(1) "Handbook of Chemistry and Physics," 44th ed., p 1694, Chemical Rubber Publ. Co., Cleveland, Ohio, 1962.

- (2) Lietzke, M. H., Stoughton, R. W., *J. Amer. Chem. Soc.*, **78**, 3023 (1956).  
(3) Lietzke, M. H., Stoughton, R. W., *J. Phys. Chem.*, **63**, 1183 (1959).  
(4) Lietzke, M. H., Stoughton, R. W., Young, T. F., *ibid.*, **65**, 2247 (1961).  
(5) McKinney, W. A., Evans, L. G., Simpson, W. W., "Recovery of Copper from Crushed and Sized Proprietary Mine Waste," paper presented at AIIME Annual Meeting, Denver, Colo., February 1970.  
(6) Sheffer, H. W., Evans, L. G., U.S. Bureau of Mines IC 8341, 1968.

Received for review April 1, 1974. Accepted July 23, 1974.

# Vapor-Liquid Equilibrium of Binary Mixtures of Butyl Alcohols with Triethylamine

Kil W. Chun,<sup>1</sup> Joseph C. Drummond,<sup>2</sup> William H. Smith, and Richard R. Davison<sup>3</sup>  
*Department of Chemical Engineering, Texas A&M University, College Station, Tex. 77843*

**Pressure-composition and excess free energies are given for binary mixtures of primary, secondary, and tertiary butyl alcohols with triethylamine at temperatures from 10° to 40°C.**

This is the third in a series of reports on the properties of binary mixtures of triethylamine with saturated aliphatic alcohols (1, 2). As with most mixtures involving strong hydrogen bonds, the excess functions are quite dependent upon alkyl substitution near the hydrogen bonding group. Vapor-liquid equilibrium of the *n*-butanol-triethylamine system has been reported previously at higher temperatures (3).

## Experimental

The vapor-pressure apparatus has been described previously (4). In brief, the apparatus consists of detachable glass sample flasks that allow the sample to be degassed without change in composition. Two of these sample flasks are joined to a glass manifold by ball joints so that two samples can be run at once. The manifold consists of three ball-jointed sections which connect the sample flasks to mercury manometers. The manometer legs not in contact with sample vapors are connected to a common section of the manifold. Vacuum stopcocks are connected to each of the three sections of the glass manifold and are, in turn, connected by ball joints and flexible hoses to an external vacuum manifold. Connections from the external manifold lead to a vacuum pump, McLeod gage, and an external manometer.

Samples of approximately the desired compositions are made up by weight and transferred to the sample flasks through their stopcock bore by a hypodermic syringe equipped with a long needle. After degassing, the flasks are connected to the evacuated glass manifold.

The glass apparatus, consisting of flasks, manometers, stopcocks, and connecting pieces, is suspended in a constant temperature bath and can be agitated to hasten equilibrium. The submerged manometers are read in the bath with a cathetometer. For pressures that do not ex-

ceed the length of the manometers (about 130 mm), a high vacuum can be maintained in the center section between the manometers, and the pressures can be read directly. For higher pressures a back pressure, which can be measured on the external manometer, must be maintained in the vacuum manifold and the center section. The pressures were read with a cathetometer to 0.05 mm. The measurements involved two or four readings, however, and errors up to 0.2 mm could easily result. The readings were corrected for temperature and gravity. The correction for vapor density is not significant.

A uniform bath temperature was maintained by a circulating pump, and the temperature was controlled to within 0.01°C by a thermistor-actuated proportional temperature controller. The temperature was measured with a calibrated glass thermometer, and recorded temperatures are accurate within 0.03°C. An error of 0.03°C would cause a maximum pressure error of 0.2 mm for the alcohol-triethylamine systems at 40°C.

Chemical analysis of the liquid phase was by acid titration of the amine except at amine concentrations in excess of 90% by weight in which case gas chromatography gave better results. The titrations were carried out as follows. The sample was slowly injected into 1*N* HCl until the pH reached 2. Then the excess acid was titrated with 1*N* THAM (tris-hydroxymethyl amino methane) to an end point of 4.7. The acid was standardized against purified amine, and the THAM against the acid. Reproducibility was about 1 part in 500 of amine. The analyses were made in triplicate, and more were made if agreement was not within 1 part in 500. The gas chromatograph used at high amine content contained a 20-ft by 1/4-in. column packed with Fluoropak with a silicone coating. The chromatographic analyses were run at least four times and usually more, and the results were compared with known samples made by weight. Accuracy is believed to be within 0.2 mol %.

All materials were distilled from commercial products on a Stedman column at high reflux. A cut with a boiling range of not more than 0.1°C was used. Triethylamine and *n*-butyl alcohol showed a single peak on the gas chromatograph. Secondary and tertiary butyl alcohol showed a small additional peak amounting to about 0.2%. The samples were collected and stored under nitrogen. They were withdrawn through the stopcock bore with a hypodermic needle and transferred to the sample

<sup>1</sup> Present address, Korean Institute of Science and Technology, Seoul, Korea.

<sup>2</sup> Present address, Olin Corp., Pasadena, Tex.

<sup>3</sup> To whom correspondence should be addressed.

**Table I. Measured Total Pressures (mm Hg)**

Mol % amine	Temp, °C			
	10	20.05	30.05	40
Triethylamine- <i>n</i> -butyl alcohol				
0	2.25	4.6	9.75	18.7
8.90	3.85	7.7	15.15	27.45
16.85	6.3	11.85	21.4	37.25
27.52	9.5	17.95	31.1	51.3
35.35	12.4	22.5	38.2	62.4
45.13	15.8	27.65	46.7	75.25
50.85	17.9	31.1	51.4	82.1
59.56	20.45	35.05	57.15	90.5
72.57	23.8	40.4	66.0	103.1
80.10	26.2	44.05	71.5	112.1
87.22	28.2	47.2	76.25	119.05
94.09	29.7	50.45	80.45	125.15
100.00	31.3	52.4	84.65	130.4
Triethylamine-sec-butyl alcohol				
0	5.85	12.3	24.25	45.1
8.74	7.8	16.1	30.45	54.95
17.40	11.25	21.0	38.05	65.8
27.27	13.75	25.55	45.2	76.15
36.87	17.0	30.4	52.25	86.35
45.57	18.8	33.8	57.5	93.55
55.39	21.35	37.65	63.2	101.9
64.51	23.3	40.25	67.4	107.15
72.71	25.4	43.8	71.85	113.55
79.97	26.65	45.8	74.95	117.95
86.88	27.95	47.85	78.2	121.3
93.93	29.45	50.05	80.9	124.2
100.00	31.3	52.4	84.65	130.4
Triethylamine-tert-butyl alcohol				
	25.0°C	30.05°C	40.0°C	
0	42.0	57.4	102.45	
9.76	48.9	65.85	114.7	
71.25	53.2	71.35	122.05	
27.49	58.3	77.0	129.3	
36.20	61.45	81.15	134.5	
45.59	64.05	83.9	138.7	
55.54	66.35	86.4	141.25	
64.42	67.75	87.9	142.9	
72.55	68.95	88.85	142.85	
79.04	69.15	88.9	142.15	
87.08	69.25	88.6	140.05	
91.23	69.0	87.85	138.8	
100.00	66.75	84.65	130.4	

flasks, also filled with nitrogen, in the same manner. The boiling points of the pure materials at 760 mm were: triethylamine, 89.55°C; *n*-butyl alcohol, 117.35°C; sec-butyl alcohol, 98.95°C; and tert-butyl alcohol, 82.4°C. This compares with reported values of 89.55 (3) for triethylamine, 117.66 (7) for *n*-butyl alcohol, 99.55 (7) for sec-butyl alcohol, and 82.42 (7) for tert-butyl alcohol.

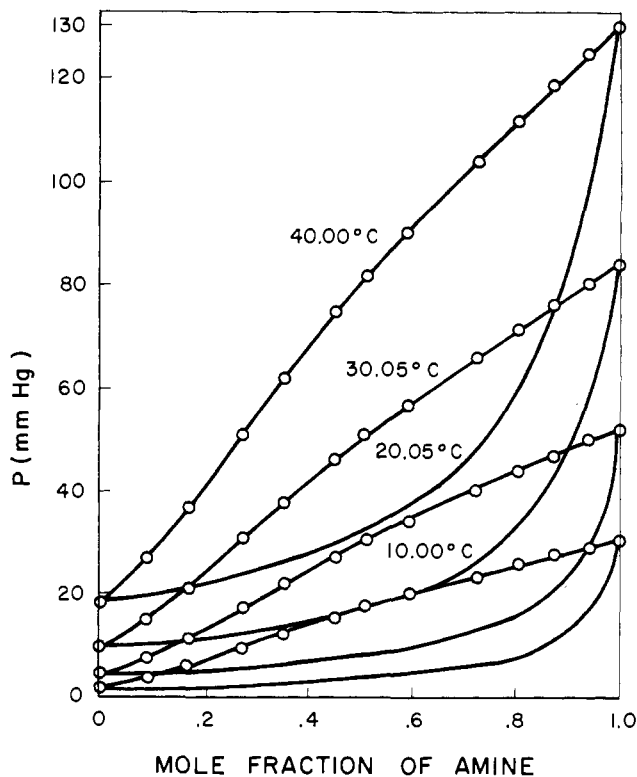
**Calculation of Vapor Compositions**

The vapor composition and activity coefficients were calculated by the total pressure method in which the Gibbs-Duhem equation is integrated numerically with the total pressure-liquid composition data. The Gibbs-Duhem equation was expressed in the form

$$\ln \gamma_2 = -\frac{x_1}{x_2} \ln \gamma_1 + \int_0^{x_1} \frac{\ln \gamma_1}{x_2^2} dx_1 \quad (1)$$

**Table II. Results of Numerical Integration of Total Pressure-Liquid Composition Data**

$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$g^E$ , cal/mol	$P$ , mm
Triethylamine(1)- <i>n</i> -butyl alcohol(2) at 10°C					
0	0	0.455	1.000	0	2.25
0.1	0.528	0.708	0.980	-29.7	4.19
0.2	0.759	0.858	0.948	-41.3	7.07
0.3	0.863	0.961	0.913	-42.4	10.46
0.4	0.916	1.033	0.879	-36.2	14.11
0.5	0.945	1.060	0.862	-25.6	17.55
0.6	0.963	1.059	0.863	-13.8	20.66
0.7	0.975	1.045	0.885	-3.2	23.49
0.8	0.984	1.028	0.932	4.4	26.15
0.9	0.992	1.013	1.018	7.4	28.75
1.0	1.000	1.000	2.817	0	31.30
Triethylamine(1)- <i>t</i> -butyl alcohol(2) at 30.05°C					
0	0	1.800	1.000	0	57.40
0.1	0.215	1.676	1.003	32.9	66.06
0.2	0.359	1.544	1.018	60.9	72.95
0.3	0.464	1.432	1.044	83.1	78.40
0.4	0.544	1.322	1.090	98.4	82.39
0.5	0.608	1.222	1.162	105.8	85.19
0.6	0.667	1.144	1.261	104.5	87.13
0.7	0.734	1.096	1.363	94.6	88.48
0.775	0.788	1.069	1.459	82.6	89.08
0.775	0.767	1.042	1.614	84.0	89.08
0.8	0.791	1.040	1.614	76.7	89.04
0.9	0.876	1.017	1.897	47.6	88.38
1.0	1.000	1.000	2.700	0	84.65



**Figure 1.** Pressure-composition data for *n*-butyl alcohol and triethylamine

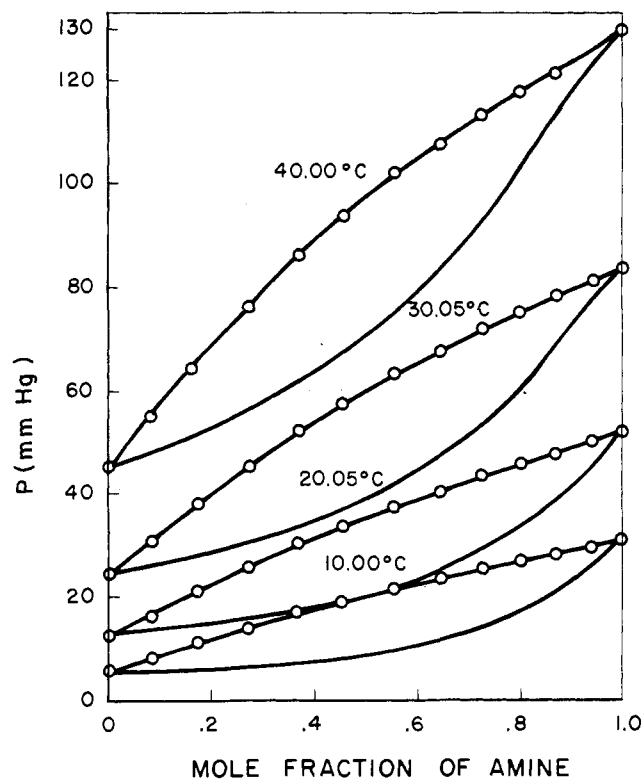


Figure 2. Pressure-composition data for sec-butyl alcohol and triethylamine

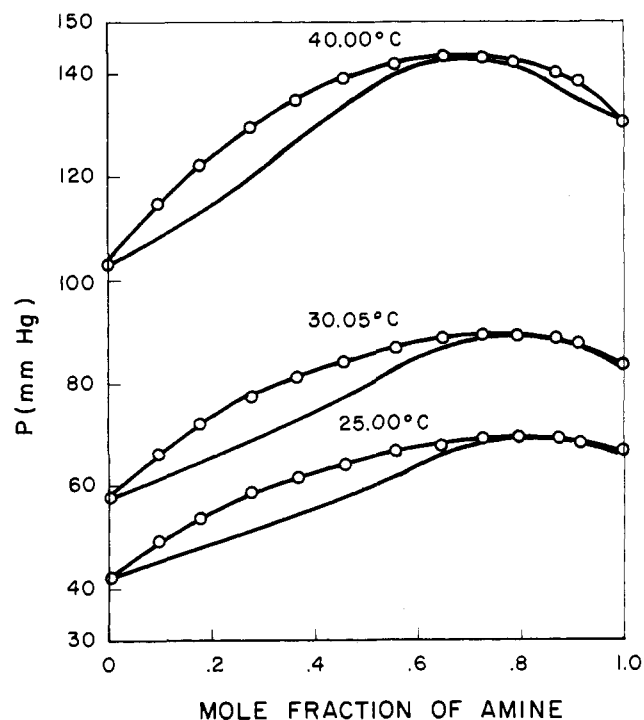


Figure 3. Pressure-composition data for tert-butyl alcohol and triethylamine

which involves the assumption that the activity coefficient is independent of pressure.

The data in Table I were plotted on large graph paper, and values of the total pressure were interpolated at mole fraction intervals of 0.025. Equation 1 was integrated using Simpson's rule and solved simultaneously with the equation

$$P = P_1^\circ \Phi_1 \gamma_1 x_1 + P_2^\circ \Phi_2 \gamma_2 x_2 \quad (2)$$

in which  $\Phi$  is the ratio of the fugacity coefficient of the pure component vapor to the fugacity of the component in the vapor mixture. The fugacity coefficients were calculated as proposed by Prausnitz et al. for polar compounds (6). Actually, the correction for vapor-phase non-ideality is practically insignificant. Numerical integration in each instance proceeded in the direction of increasing pressure. Details of the numerical procedures have been given elsewhere (5).

## Results

Sample results for triethylamine-*n*-butyl alcohol at 10°C and triethylamine-*tert*-butyl alcohol at 30°C are given in Table II. The last digit in the pressure in Table II is not significant but is included to reduce computer roundoff error. Figures 1-3 show total pressure-liquid composition and calculated vapor compositions. The data in Table II for *tert*-butyl alcohol show mismatch at the azeotrope. Extreme sensitivity of the integrated function to small pressure perturbations is exhibited as the azeotrope is approached. The function becomes indeterminate at the azeotrope.

The excess free energies calculated by numerical integration of the total pressure-composition curves were fitted with a polynomial of the form

$$\frac{g^E}{RTx_1x_2} = \sum_{j=0}^5 a_j x_1^j \quad (3)$$

Table III. Constants for Polynomial Representation of  $g^E$ , cal/mol

$$g^E/RTx_1x_2 = \sum_{j=0}^5 a_j x_1^j$$

Temp, °C	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$
Triethylamine(1)- <i>n</i> -butyl alcohol(2)						
10.0	-0.80386	2.8690	-8.8888	19.8422	-21.5831	8.9194
20.05	-0.36494	0.1642	1.2749	1.7329	-6.7989	4.5169
30.05	-0.35042	1.2200	-3.2710	9.1188	-11.4505	5.1315
40.0	-0.18270	0.1085	1.1522	1.6138	-6.2004	4.0871
Triethylamine(1)- <i>sec</i> -butyl alcohol(2)						
10.0	-0.16986	1.4626	-0.3632	-5.7775	10.3124	-5.3792
20.05	-0.05340	0.9641	0.9811	-7.7682	12.0324	-5.8823
30.05	0.08824	0.2200	2.6979	-8.8288	11.0484	-4.8492
40.0	0.22320	0.0747	3.0078	-11.7209	17.5652	-9.1242
Triethylamine(1)- <i>tert</i> -butyl alcohol(2)						
25.0	0.60865	-0.7070	6.1406	-16.1635	18.4203	-7.4020
30.05	0.58636	0.1425	0.7678	-1.9103	1.4883	-0.0725
40.0	0.59077	0.6525	-3.3737	9.9042	-12.5069	5.8779

The constants are given in Table III, and the average and maximum deviation for the polynomials is given in Table IV both for  $g^E$  and for total pressures calculated using the polynomials. The deviations are probably within the confidence limit of the data.

It is difficult to estimate the errors in  $g^E$  from errors in the total pressure curve since the former were obtained indirectly, but changes in  $g^E$  obtained by perturbations in the pressure values of less than 0.2 mm indicate that the error is within 1-2 cal/mol.

**Table IV. Error in Using Polynomial Expansion**

Temp, °C	Average error		Maximum error	
	$g^E$ , cal/mol	P, mm	$g^E$ , cal/mol	P, mm
Triethylamine- <i>n</i> -butyl alcohol				
10.0	0.16	0.03	0.39	0.08
20.05	0.46	0.13	1.30	0.47
30.05	0.16	0.08	0.31	0.19
40.0	0.23	0.15	0.44	0.38
Triethylamine-sec-butyl alcohol				
10.0	0.26	0.05	0.64	0.12
20.05	0.34	0.09	0.78	0.23
30.05	0.30	0.13	0.71	0.34
40.0	0.47	0.27	0.93	0.60
Triethylamine-tert-butyl alcohol				
25.0	0.27	0.09	0.78	0.25
30.05	0.18	0.12	0.57	0.22
40.0	0.28	0.20	2.26	0.39

**Nomenclature**

$a_j$  = constants in Equation 3  
 $f$  = fugacity  
 $g^E$  = molar excess Gibbs free energy, cal/g-mol  
 $P$  = total pressure, mm Hg

$x$  = liquid mole fraction  
 $y$  = vapor mole fraction

**Greek Letters**

$\gamma$  = activity coefficient =  $f/f^0x$   
 $\Phi$  = ratio of the fugacity coefficient of a pure component to the component fugacity coefficient in the mixture

**Subscripts**

1 = more volatile component or amine  
 2 = less volatile component or alcohol

**Superscripts**

$^0$  = pure component

**Literature Cited**

- (1) Chun, K. W., Davison, R. R., *J. Chem. Eng. Data*, **17**, 307 (1972).
- (2) Chun, K. W., Drummond, J. C., Davison, R. R., *ibid.*, in press.
- (3) Copp, J. L., Findlay, T. J. V., *Trans. Faraday Soc.*, **56**, 13 (1960).
- (4) Davison, R. R., Smith, W. H., Chun, K. W., *AIChE J.*, **13**, 591 (1967).
- (5) Davison, R. R., Smith, W. H., Chun, K. W., *Chem. Eng. Sci.*, **24**, 589 (1969).
- (6) Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor Liquid Equilibria," Prentice-Hall, Englewood Cliffs, N.J., 1967.
- (7) Wilhoit, R. C., Zwolinski, B. J., "Physical and Thermodynamic Properties of Aliphatic Alcohols," Thermodynamic Research Center, Texas A&M University, *J. Phys. Chem. Ref. Data*, **2**, Suppl. No. 1 (1973).

Received for review April 10, 1974. Accepted August 5, 1974.

# Enthalpies of Mixtures of Polar and Nonpolar Component: System *n*-Pentanol-*n*-Heptane

Tran P. Thinh,<sup>1</sup> Rubens S. Ramalho, and Serge C. Kaliaguine<sup>2</sup>

Department of Chemical Engineering, Laval University, Quebec, Que., Canada G1K 7P4

Enthalpy data were measured for mixtures of *n*-pentanol and *n*-heptane containing 0.250, 0.500, and 0.750 mole fraction *n*-pentanol. The measurements covered the range from 100 to 1000 psia and 350–600°F and included the liquid, vapor, vapor-liquid, and critical regions. The experimental results in the vapor phase were compared with values calculated by two methods for prediction of variation of enthalpy with pressure, those of Lydersen and Storvick.

To test and develop methods for prediction of enthalpy of nonideal mixtures, direct enthalpy measurements were carried out for the *n*-pentanol-*n*-heptane system as a function of composition (0.250, 0.500, 0.750 mole fraction *n*-pentanol), temperature (350–600°F), and pressure (100–1000 psia). No generalized and adequate method for prediction of enthalpy of nonideal solutions is yet available (7).

For a few *n*-alcohol-hydrocarbon systems (benzene-

methanol, benzene-ethanol, *n*-pentane-ethanol) McCracken et al. (3) and Storvick and Smith (9–11) have proposed a correlating procedure based upon association of the alcohol.

This paper presents enthalpy data as well as an evaluation of the methods for prediction of enthalpy of Lydersen et al. (2) and Yen and Alexander (15), and McCracken et al. (3) and Storvick and Smith (9–11).

**Experimental**

The flow calorimeter utilized in this work, as well as the experimental procedure followed, have been described previously (12). The *n*-pentanol and *n*-heptane used were from Fisher Scientific Co., respectively, of lot 716063, with a boiling range of 137.7–138.0°C, and lot 785040 with certified spectroanalysis. Evaluation of the apparatus performance with pure *n*-pentane has been discussed in the previous article (12), an error analysis indicating the overall possible error on the measured enthalpy values to be ±1.1 Btu/lbm. Enthalpy data for pure *n*-pentanol and *n*-heptane have been reported in previous work (12, 13).

**Principles of Enthalpy Determinations**

The enthalpy is determined by measuring the energy transferred from the test fluid to the boiling Freon-11. The enthalpy

<sup>1</sup> Present address, Laboratoire Central, Ministère des Transports, Complexe Scientifique du Québec, 555 Boulevard Henri IV, Québec, Que., Canada G1V 4C7.

<sup>2</sup> To whom correspondence should be addressed.