Vapor-Liquid Equilibrium of Binary Mixtures of Triethylamine with Propyl and Isopropyl Alcohol

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Pressure-composition, excess free energies, and excess enthalpies are given for binary mixtures of triethylamine with propyl alcohols from 10° to 40°C.

Earlier work in this series on hydrogen-bonding solutions have included various water-amine binaries (*3, 5*) and triethylamine with methyl and ethyl alcohol (*1*). These solutions are often characterized by large negative heats of solutions and excess entropies. In the present work, the data are extended to triethylamine with the propyl alcohols. *n*-Propyl alcohol-triethylamine has been previously investigated (*2*) at higher temperatures.

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 exceed 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 accuated 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 both 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 wt % 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 ¼-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. All samples used showed a single peak on the gas chromatograph. The samples were collected and stored under nitrogen. They

Table I. Measured Total Pressures
Pressures in mm of Hg

Mol % amine	Temp, °C 10	20.05	30.05	40
	Triethylamine–*n*-propyl alcohol			
0	7.55	15.2	28.7	52.2
8.38	8.6	17.5	33.15	58.8
17.11	11.25	21.3	39.15	67.8
27.87	14.25	26.25	46.6	78.85
37.17	16.95	30.45	53.05	88.15
45.81	19.2	34.2	58.45	95.8
55.08	21.25	37.75	63.5	103.2
66.25	24.2	42.05	69.4	110.75
72.36	25.55	43.7	72.6	114.95
75.48	26.3	44.65	73.6	116.85
86.77	28.05	47.75	78.55	123.15
94.10	29.85	50.15	81.3	126.75
100.0	31.3	52.4	84.65	130.4
	Triethylamine–isopropyl alcohol			
0	16.15	31.6	59.05	103.8
7.16	18.4	...	63.8	111.25
14.22	20.1	38.1	68.1	117.65
21.78	22.55	41.7	73.0	124.25
28.84	23.85	43.9	76.35	128.45
33.59	25.0	46.3	78.85	131.85
42.92	26.55	48.05	81.85	136.65
50.66	27.85	49.4	83.95	139.35
56.36	28.2	50.45	85.55	140.65
64.75	29.25	51.95	86.85	142.1
73.77	29.95	52.55	87.55	142.05
82.44	30.6	53.1	87.75	141.05
92.34	31.0	53.1	87.0	137.7
100.0	31.3	52.4	84.65	130.4

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were withdrawn through the stopcock bore with a hypodermic needle and transferred to the sample flasks, also filled with nitrogen, in the same manner. The boiling points of the pure material at 760 mm were: triethylamine, 89.55°C, *n*-propyl alcohol, 97.15°C, and isopropyl alcohol, 82.2°C. These values agree closely with reported values of 89.55–89.59°C (*2*), 97.20 and 82.26°C (*7*).

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

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

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 by using Simpson's rule and solved simultaneously with the equation

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

in which Φ 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 nonideality is practically insignificant. Numerical integration in each instance proceeded from each pure component to the azeotrope. Details of the numerical procedures have been given elsewhere (*5*).

Results

A sample result for triethylamine–isopropyl alcohol is shown in Table II. The last digit in the pressures in Table II is not significant but is included to reduce computer roundoff error. The total pressures vs. liquid compositions are given in Table I. Figures 1 and 2 show total pressure-liquid compositions and calculated vapor compositions.

The results in Table II show the error that results near the azeotrope and over very flat regions. Note the mismatch at the azeotrope and the obviously bad value at $x_1 = 0.9$. In Figure 2 at this temperature, dP/dx is very small from about $x_1 = 0.7$ to 1.0 and 0 at the azeotrope. The integrated function is indeterminate at the azeotrope and thus subject to error in this neighborhood. Calculated results for isopropyl alcohol at 30°C are not given because they are inconsistent with the other temperatures when g^E/T is plotted vs. $1/T$. The slope of such a plot is h^E, and values for *n*-propyl alcohol at 25°C calculated in this manner are shown in Figure 3.

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

Triethylamine = one, isopropyl alcohol = two at 20.05°C

x_1	y_1	γ_1	γ_2	g^E	P
0	0.000	1.535	1.000	0.00	31.59
0.05	0.117	1.521	1.000	12.26	34.00
0.1	0.217	1.502	1.001	24.35	36.35
0.2	0.374	1.452	1.008	46.94	40.70
0.3	0.487	1.372	1.027	65.99	44.29
0.4	0.574	1.291	1.060	80.05	47.19
0.5	0.645	1.200	1.111	88.56	49.53
0.6	0.702	1.142	1.204	89.57	51.13
0.7	0.757	1.079	1.336	81.86	52.28
0.8	0.823	1.041	1.487	64.75	53.03
0.85	0.854	1.020	1.639	53.20	53.23
0.85	0.843	1.007	1.791	54.46	53.23
0.9	0.897	1.011	1.726	37.89	53.17
1.0	1.000	1.000	2.122	0.00	52.39

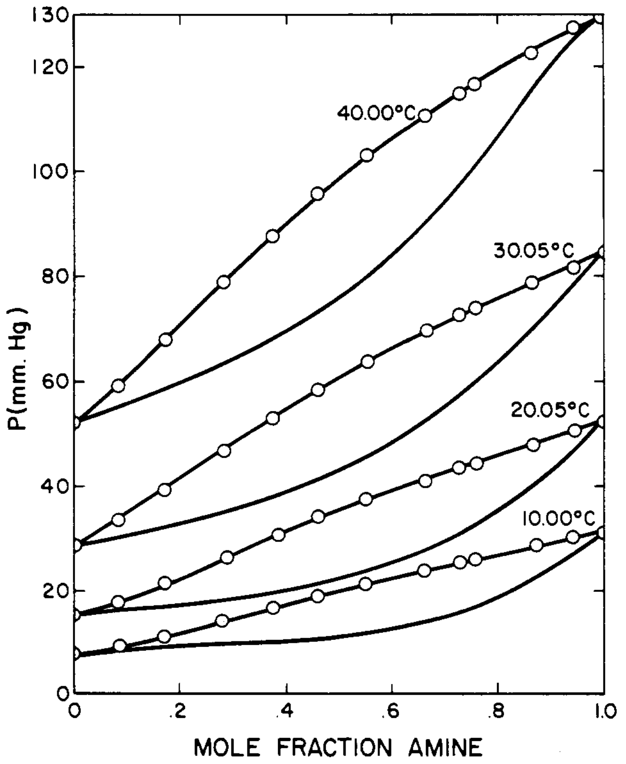

Figure 1. Pressure-composition data for *n*-propyl alcohol–triethylamine

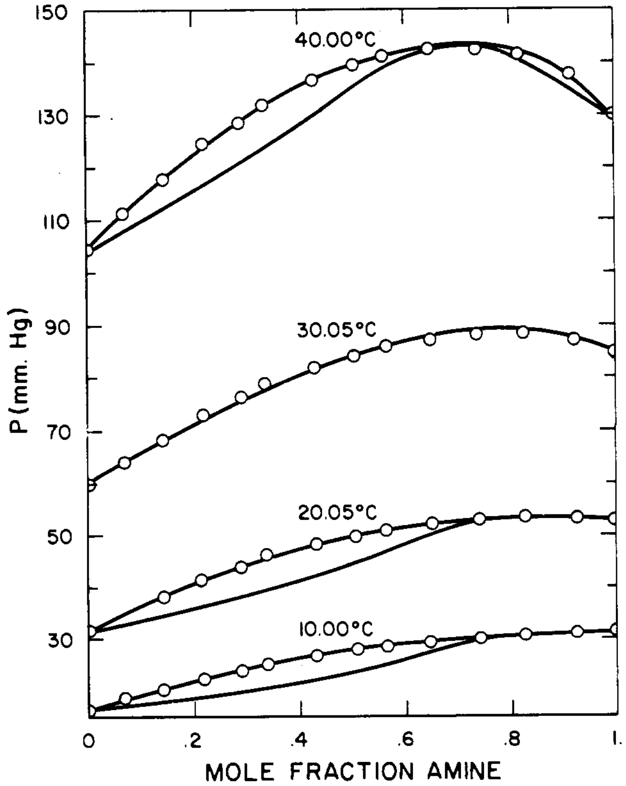

Figure 2. Pressure-composition data for isopropyl alcohol–triethylamine

Table III. Constants for Polynomial Representation

Molar Gibbs excess free energy

$$g^E/RTx_1x_2 = \sum_{j=0}^{n} a_j x$$

Temp, °C	a_0	a_1	a_2	a_3	a_4	a_5
			Triethylamine(1)–*n*-propyl alcohol(2)			
10.0	−0.89419	4.1312	−7.2837	4.7524	2.1366	−2.8303
20.05	−0.28322	0.3974	5.0203	−17.9795	24.2824	−11.4835
30.05	−0.08384	0.1552	2.5187	−5.6437	4.8601	−1.4266
40.0	−0.08299	0.0865	5.6236	−17.5111	21.5042	−9.3772
			Triethylamine(1)–isopropyl alcohol(2)			
10.0	0.35677	0.7618	−2.4426	7.1529	−9.1549	3.8508
20.05	0.42375	0.4246	−0.1534	0.0830	0.0259	−0.0562
40.0	0.53496	−0.1773	1.0424	0.6046	−3.1506	2.1316

Table IV. Error in Using Polynomial Expansion

	n-Propyl alcohol				Isopropyl alcohol			
	Av error		Max error		Av error		Max error	
Temp	g^E	P	g^E	P	g^E	P	g^E	P
10	0.27	0.05	0.75	0.13	0.24	0.04	0.64	0.13
20	0.20	0.06	0.51	0.21	0.17	0.07	0.61	0.14
30	0.25	0.12	0.70	0.31				
40	0.43	0.24	1.05	0.63	0.19	0.15	1.65	0.28

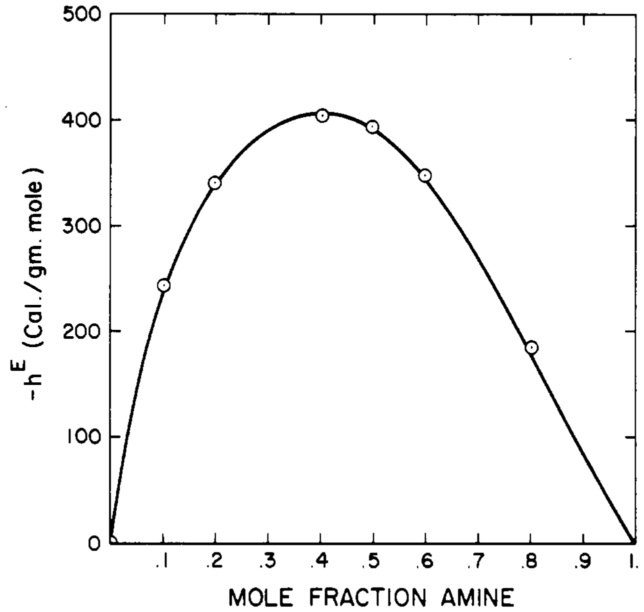

Figure 3. Heat of mixing of *n*-propyl alcohol–triethylamine at 25°C

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

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

The constants are given in Table III, and the average and maximum deviations for the polynomials are given in Table IV both for g^E and for total pressures calculated with 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 small perturbations in the pressure values indicate that the error is within 1-2 cal/mol. Of course, error in the h^E values could be an order of magnitude larger.

Nomenclature

a_j = constants in Equation 3
f = fugacity
g^E = molar excess Gibbs free energy in cal g-mol
h^E = molar excess enthalpy in cal g-mol
P = total pressure in mm Hg
x = liquid mole fraction
y = vapor mole fraction

Greek

γ = activity coefficient = $f/f^{\circ}x$
Φ = 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

° = pure component

Literature Cited

(1) Chun, K. W., Davison, R. R., *J. Chem. Eng. Data*, **17**, 307 (1972).
(2) Copp, J. L., Findlay, T. J. V., *Trans. Faraday Soc.*, **56**, 13 (1960).
(3) Davison, R. R., *J. Chem. Eng. Data*, **13**, 348 (1968).
(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*, Supp. No. 1, Vol 2 (1973).

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