Thermodynamic Properties of Binary Mixtures of Triethylamine with Methyl and Ethyl Alcohol

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Pressure composition, excess free energies, and excess enthalpies are given for binary mixtures of triethylamine with methyl and ethyl alcohol from 10–40°C.

Earlier works in this series (*5–8*) on hydrogen bonding solutions have reported data on amine–water solutions. This work extends the study to alcohol–amine systems. The strong hydrogen bond which exists between an OH group and the amine nitrogen usually results in negative heats of mixing and, for partially miscible systems, lower critical solution temperatures.

Both of these triethylamine–alcohol systems have been studied previously (*3, 4*) but at higher temperatures, though in each case the highest temperature in this work corresponds to the lowest in the previous studies. The temperature range reported here corresponds to that in previous work in this series.

EXPERIMENTAL METHODS

The vapor pressure apparatus and experimental methods have been described previously (*5, 7*) but the glass manifold has been modified to eliminate the ball joint on the manometer leg that was in contact with sample vapor. This makes apparatus cleaning more difficult, but it eliminates the main source of trouble in the apparatus.

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-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 0.4 mm for methyl alcohol–triethylamine at 40°C decreasing to 0.2 mm at 30°C. For the ethyl alcohol–triethylamine system, the maximum error would be about 0.2 mm at 35°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 (trishydroxymethyl 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. All samples used showed a single peak on the gas chromatograph. The samples were collected and stored under nitrogen. They 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, methyl alcohol 64.6°C, and ethyl alcohol 78.3°C.

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

$$\ln \gamma_2 = -\frac{x_1}{x_2} \ln \gamma_1 + \int_0^{x_1} \frac{\ln \gamma_1}{x_2^2}\, dx_1 \tag{1}$$

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

The data in Table I were plotted on large graph paper, and

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Table I. Measured Total Pressures

(Pressures in mm of Hg)

Mol % alcohol	Temp, °C 10	20.05	30.05	40
	Triethylamine-Methyl Alcohol			
0	31.3	52.4	84.65	130.4
4.74	33.7	57.4	94.15	147.55
8.57	36.0	61.85	100.75	158.8
17.22	38.55	66.7	109.95	175.45
29.52	42.25	73.45	122.9	...
42.24	44.2	78.0	132.0	214.3
55.81	46.0	81.05	137.55	224.55
56.49	46.35	82.2	137.35	225.05
73.97	49.45	86.65	145.8	238.9
75.80	49.35	87.1	147.05	...
87.76	52.65	91.55	154.55	251.45
95.65	55.0	95.85	160.0	258.8
100.00	56.3	97.95	162.2	262.05
Mol % Amine	**Temp, °C 10**	**20.05**	**30.05**	**35**
	Triethylamine-Ethyl Alcohol			
0	23.55	43.95	78.6	102.55
8.57	24.05	45.6	80.65	105.15
15.20	25.15	47.05	83.15	108.65
26.56	27.0	49.75	87.0	112.75
36.17	28.7	51.85	90.25	116.0
46.54	29.55	53.35	91.95	117.9
54.34	30.75	54.95	93.6	119.25
64.67	31.15	55.1	93.5	119.15
74.50	31.85	56.1	94.8	118.55
85.03	31.75	55.5	92.6	115.75
94.94	31.9	54.55	89.55	110.2
100.00	31.3	52.4	84.65	105.55

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

(Methyl alcohol = one triethylamine = two at 20.05°C)

x_1	y_1	γ_1	γ_2	g^E	P
0.000	0.000	1.982	1.000	0.000	52.4
0.050	0.142	1.691	1.004	17.7	58.27
0.100	0.233	1.480	1.015	30.7	62.37
0.150	0.304	1.358	1.028	40.2	65.71
0.200	0.364	1.274	1.041	47.1	68.61
0.250	0.416	1.210	1.057	52.0	71.16
0.300	0.464	2.159	1.074	55.0	73.45
0.350	0.505	1.110	1.097	56.3	75.40
0.400	0.542	1.067	1.124	55.8	77.10
0.450	0.580	1.034	1.150	53.5	78.70
0.500	0.613	1.001	1.184	49.6	80.04
0.550	0.648	0.978	1.216	44.1	81.34
0.600	0.684	0.960	1.247	37.2	82.54
0.650	0.724	0.952	1.264	29.2	83.79
0.700	0.767	0.952	1.264	20.9	85.14
0.750	0.813	0.959	1.241	13.0	86.68
0.800	0.858	0.967	1.206	5.9	88.38
0.850	0.900	0.976	1.151	0.3	90.33
0.900	0.940	0.987	1.067	−3.0	92.63
0.950	0.974	0.996	0.958	−3.4	95.22
1.000	1.000	1.000	0.777	0.000	97.95

values of the total pressure were interpolated at mole fraction intervals of 0.025. Water vapor pressures were taken from Lange (*13*). Equation 1 was integrated using Simpson's rule and solved simultaneously with the equation

$$P = P_1^0\Phi_1\gamma_1x_1 + P_2^0\Phi_2\gamma_2x_2 \qquad (2)$$

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. (*14*) for polar compounds. Actually the correction for vapor phase nonideality is practically insignificant. Details of the numerical procedures have been given elsewhere (*8*).

RESULTS

A sample result for methyl alcohol–triethylamine at 20.05°C 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 data and calculated vapor compositions.

A comparison of the pressures obtained in this work and by Copp and Findlay (*4*) for triethylamine–methyl-alcohol is shown in Figure 3. It can be seen that Copp and Findlay's values at the alcohol-rich end are higher than our values. Table III is a comparison of pure component vapor pressures from various sources for all the pure components.

The function g^E/RTx_1x_2 was fitted with Tchebychef polynomials as described by Birge (*2*), and from these results power series of the form

$$\frac{g^E}{RTx_1x_2} = \sum_{j=0}^{n} a_jx_1^j$$

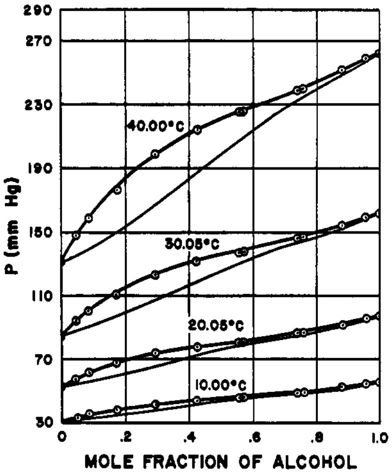

Figure 1. Vapor pressures of methyl alcohol–triethylamine solutions

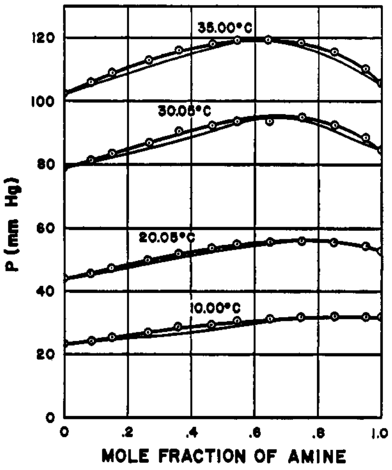

Figure 2. Vapor pressures of ethyl alcohol–triethylamine solutions

Table III. Comparison of Vapor Pressures of Pure Materials by Various Workers

[P (mm of Hg) to nearest 0.05 mm]

Methyl Alcohol

Temp, °C	This work	Young (*17*)	Eubank (*10*)	Critical Tables (*11*)	Copp and Findlay (*4*)	Scatchard et al. (*16*)	Dever et al. (*9*)
10	56.3	54.7	54.1^a	54.0^a			
20.05	97.95	96.25^b	95.9^a	94.4^a			98.0^a
30.05	162.2	160.4^b	162.2^a	158.5^a		164.25^a	
40	262.05	260.5	263.2^a	257.0^a	265.7^b	265.8^a	264.35^a

Ethyl Alcohol

Temp, °C	This work	Young (*17*)	Scatchard and Raymond (*15*)	Kretschmer and Wiebe (*12*)	Barker et al. (*1*)	Critical Tables (*11*)	Copp and Everett (*3*)
10	23.55	23.75		23.55^a	23.3^a	23.6	
20.05	43.95	44.15^b		43.6^a	43.95^a	44.0^b	
30.05	78.6	78.3^b		78.65^a	78.6^a	79.0^b	
35	102.55		103.1^a	103.15^a	103.1^a	103.7	105.4^b

Triethyl Amine

Temp, °C	This work	Copp and Findlay (*4*)
10	31.3	31.4^a
20.05	52.4	52.6^a
30.05	84.65	84.5^a
35	105.55	105.4^a
40	130.45	129.5^a

[a] Calculated from equations. [b] Small correction for temperature variation.

Table IV. Constants for Polynomial Representation of Excess Free Energies

Methyl Alcohol (1)–Triethylamine (2)

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

Temp, °C	a_0	a_1	a_2	a_3	a_4
10	0.48730	−0.05984	−2.1171	3.4442	−2.1426
20.05	0.68952	−1.2377	2.1889	−2.6439	0.78153
30.05	0.72345	−1.4031	4.1406	−6.4413	3.1255
40	0.74292	−1.0097	3.0127	−4.9400	2.4717

Ethyl Alcohol (2)–Triethylamine (1)

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

Temp, °C	a_0	a_1	a_2	a_3	a_4
10	−0.07527	1.5353	−3.0608	3.9156	−1.6833
20.05	0.17590	0.54189	−0.35045	0.66809	−0.22719
30.05	0.23647	−0.04066	3.6072	−6.9319	4.2622
40	0.23424	0.60836	0.40935	−1.4931	1.0795

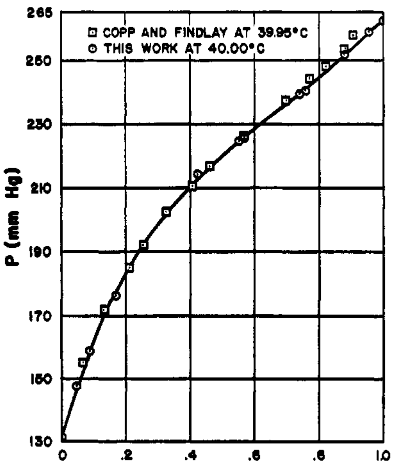

Figure 3. Vapor pressures of methyl alcohol–triethylamine solutions at 40°C

were obtained. The constants up to $n = 4$ for each case are given in Table IV. Total pressures calculated from these results show a maximum deviation from the experimental pressures as follows: methanol–triethylamine from 10–40°C, respectively, 0.37, 0.12, 0.52, and 0.79 mm and ethanol triethylamine from 10–35°C, respectively, 0.11, 0.11, 0.52, 0.17 mm. The average deviation from the experimental values is: methanol–triethylamine from 10–40°C, respectively, 0.19, 0.08, 0.21, and 0.29 mm; for ethanol–triethylamine from 10–35°C, 0.06, 0.04, 0.25, and 0.10 mm, respectively. It is difficult to estimate directly the error in g^E; however, the pressure deviations calculated from the polynomial fit are of the same order as the probable experimental errors in P. The maximum deviation in g^E, using the polynomial fit, is 2 cal/mol so that it seems probable that the absolute error is of this order also.

Values of h^E were calculated from plots of g^E/T vs. $1/T$ at various compositions. The slope of these curves is equal to minus the excess enthalpy. Values of excess enthalpy at 25°C have been calculated from these curves and combined with the excess free energy to obtain the excess entropy.

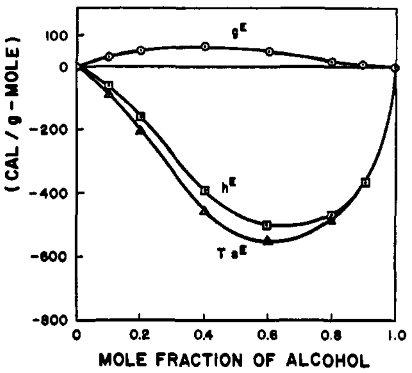

Figure 4. Excess thermodynamic functions for methyl alcohol–triethylamine at 25°C

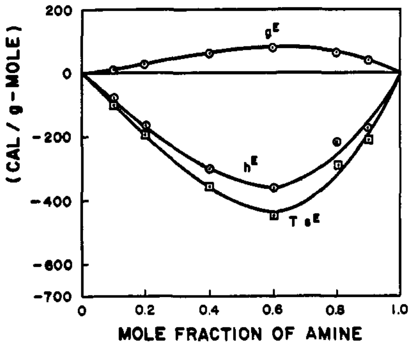

Figure 5. Excess thermodynamic functions for ethyl alcohol–triethylamine at 25°C

Values of g^E, h^E, and Ts^E at 25°C are shown in Figures 4 and 5. Errors in h^E and Ts^E could easily be 10%.

NOMENCLATURE

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 of Hg
s^E = molar excess entropy in cal/K
x = liquid mole fraction
y = vapor mole fraction

GREEK

γ = activity coefficient = f/f^0x
Φ = ratio of the fugacity coefficient of a pure component to the component fugacity coefficient in the mixture

SUBSCRIPTS

1 = more volatile component in Equations 1 and 2
2 = less volatile component in Equations 1 and 2

SUPERSCRIPTS

^{0} = pure component

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