Vapor-Liquid Equilibrium of Triethylamine–Water and Methyldiethylamine–Water

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Vapor-liquid equilibria are given for triethylamine–water at 5°, 10°, 15°, 18°, and 20°C and for methyldiethylamine–water at 10°, 20°, 30°, 35°, 40°, and 47°C.

Vapor-liquid equilibrium and total pressure data for the system triethylamine–water have been reported by a number of investigators (*9*, *10*, *12*, *14*, *15*) but with considerable disagreement. The methyldiethylamine–water system has been previously studied by Copp (*1*) at 35° and 47°C only. We have investigated these systems in a continuing study of highly nonideal hydrogen bonding solutions with emphasis on amine–water solutions (*4–6*).

EXPERIMENTAL

The experimental methods and apparatus were the same described previously (*4–7*). The apparatus was a static vapor pressure device in which the mixture sample may be degassed without change in composition. The apparatus, including the manometers, sample flasks, and glass manifold, was suspended in a constant temperature bath and could be agitated to hasten equilibrium. The pressures were measured with mercury manometers read to 0.05 mm of Hg with a cathetometer. Since the pressures being measured may exceed the manometer length (about 130 mm), a back pressure must be applied from an external source or reference solution of known vapor pressure.

In the present work, chloroform was used as reference with the methyldiethylamine system when needed. Chloroform vapor pressures (Table I) were run in the same apparatus by use of an external back pressure measured with an external mercury manometer. All manometer readings were corrected for temperature and gravity. The vapor density correction was below the measurement precision. Temperature was controlled to within 0.01°C. Temperature measurement was with a calibrated glass thermometer with 0.1°C gradations. The accuracy is believed to be within 0.03°C.

Amine analysis was by acid titration for amine concentrations less than 90 wt %. For higher concentrations gas chromatography was used. Accuracy ranged from better than 0.1 mol % at low amine concentrations to perhaps 1 mol % at the highest amine concentrations.

Table I. Vapor Pressure of Chloroform, mm of Hg

Temp, °C	This apparatus	Literature (*8*) values
10	100.4	100.5
20	158.8	159.6
30	243.9	246.0
35	299.35	301.3
40	362.4	366.4
45	434.4	439.0
47	467.9	

All pure components were obtained by repeated distillation on a Stedman column. Fractions having a boiling range of less than 0.1°C and showing a single peak on a gas chromatograph were used.

Pressure measurements with this apparatus are usually reproducible within 0.1–0.2 mm of Hg. With triethylamine–water the results were consistently poorer. Triethylamine shows an anomalous behavior previously reported (*2*, *7*) in that, above about 20°C, vapor pressures measured by static and dynamic methods diverge. This behavior is unexplained but may account for the poor reproducibility obtained for this system. Water vapor pressures were taken from Lange (*11*).

Total pressures are given in Table II and Figure 1 for triethylamine and in Table III and Figure 2 for methyldiethylamine. The triethylamine data were measured by two of the authors, and these points are differentiated. The scatter in the data is best seen in the heterogeneous region at 20°C (amine mole fractions from 0.02135–0.425) where all concen-

Table II. Experimental Vapor Pressures of Triethylamine–Water Mixtures

Mol % amine	Temp, °C 5	 10	Press, mm of Hg 15	 18	 20
0.55[a]	9.95	15.4	23.55	30.2	35.5
1.01[b]		21.8	32.8	43.45	49.2
1.08[a]	13.15	20.5	32.2	41.75	49.1
1.65[a]	16.9	26.25	40.15	50.9	59.45
2.05[b]		30.45	43.65	54.1	61.4
2.16[a]	19.2	29.3	42.15	53.35	62.1[c]
4.34[b]		31.6	44.6	54.3	61.7[c]
4.89[a]	22.1	31.8	44.95	54.75	62.25[c]
5.67[b]		31.8	45.1	54.35	61.8[c]
7.72[a]				55.0	62.3[c]
9.81[a]	23.45	33.15	45.85	55.8	62.35[c]
11.26[a]	23.45	32.95	45.8	55.6	62.5[c]
16.32[b]		33.7	45.45	55.0	62.2[c]
17.89[a]	23.8	33.5	46.1	55.45	62.55[c]
29.17[a]	25.15	34.55	46.75	55.9	62.8[c]
38.43[b]		35.45	46.9	55.7	62.2[c]
42.7[a]	25.85	34.95	46.95	55.85	62.55[c]
55.7[a]	26.4	35.6	47.6	56.55	63.45
58.68[b]		36.45	47.6	55.95	62.6
68.27[b]		36.8	48.35	56.65	63.9
77.9[a]	26.95	36.1	48.05	57.0	63.65
83.78[b]		35.9	47.6	56.5	62.6
85.6[a]	26.8	35.9	47.55	56.35	62.65
87.32[b]		36.3	47.25	55.95	62.45
89.2[a]	26.55	35.55	47.3	56.0	62.35
92.39[b]		35.15	46.45	54.6	60.9
92.9[a]	26.15	34.9	45.8	54.15	60.3
93.81[b]		34.8	45.9	53.95	55.95
95.79[b]		34.5	45.35	52.9	58.7
100.0[a]	23.85	31.35	40.65	47.55	52.65
100.0[b]		31.3	40.55	47.45	52.35

[a] Davison. [b] Chun. [c] Two liquid phases.

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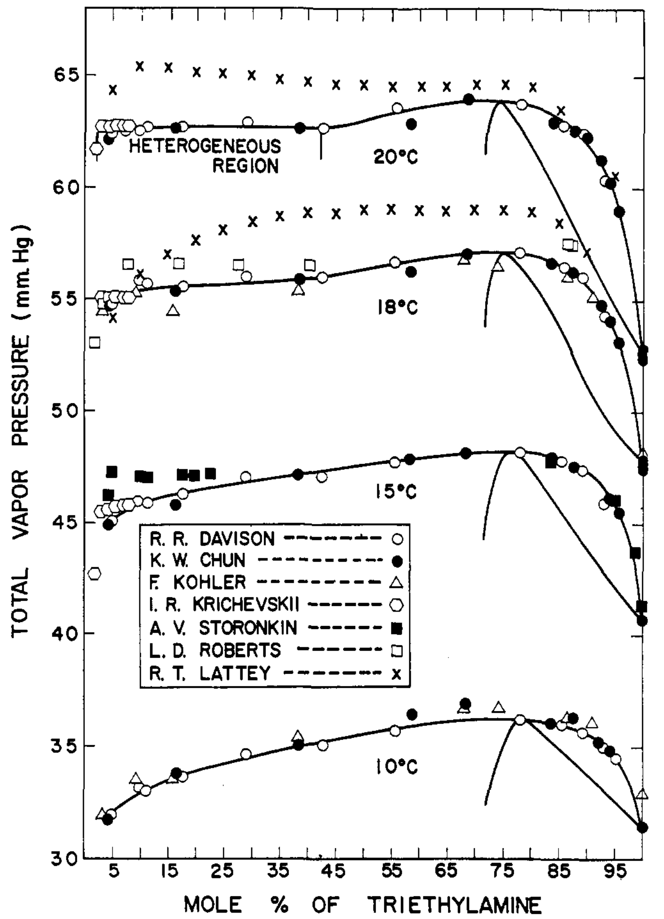

Figure 1. Pressure-composition data for triethylamine–water

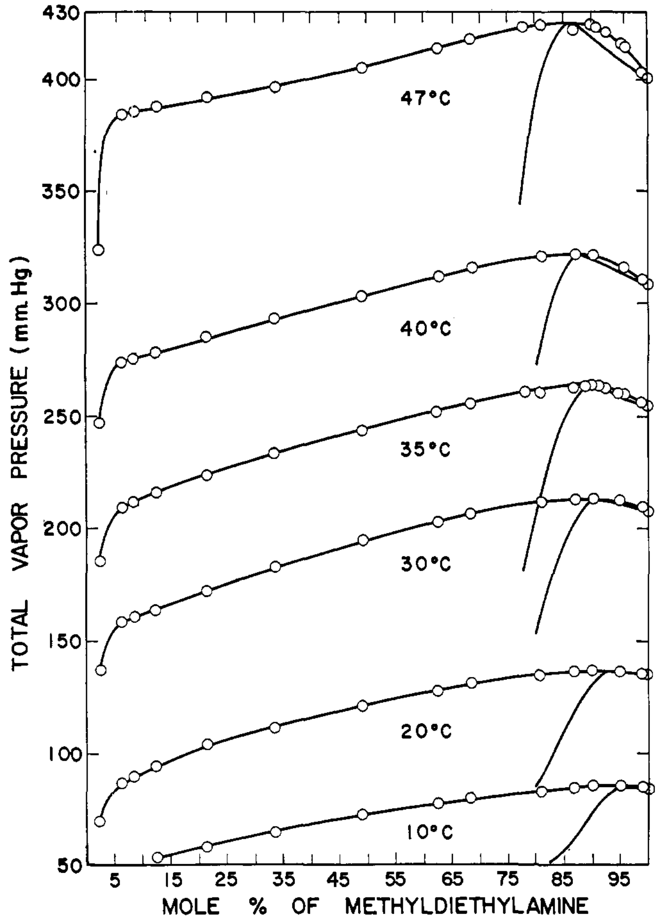

Figure 2. Pressure-composition data for methyldiethylamine–water

trations should show the same pressure. Data from several other sources are also given in Figure 1. The triethylamine-water total pressures are probably accurate within 0.5 mm of Hg. The methyldiethylamine–water total pressures show less scatter, though the absolute error could also be about 0.5 mm of Hg at 47° owing to error in temperature and pressure measurements.

Table III. Experimental Vapor Pressures of Methyldiethylamine–Water Mixtures

Mol % amine	Temp, °C 10	20	30	35	40	47
	Press, mm of Hg					
0.28	11.45	23.1	45.2	62.05	82.65	121.8
0.48	13.15	27.25	54.3	75.05	100.05	148.1
1.43	22.3	52.15	103.45	146.05	195.75	
2.37	30.9	69.1	136.3	184.65	246.3	323.55
6.25	45.3	86.3	157.5	208.55	273.85	383.7
8.41	48.95	88.8	159.75	210.55	275.25	384.9
12.43	53.2	94.2	163.5	214.9	277.75	387.45
21.48	57.75	103.0	171.7	222.9	284.1	391.4
33.40	64.85	110.95	182.35	232.9	292.7	395.7
48.97	72.55	120.65	194.1	243.15	302.95	404.7
62.50	77.25	127.45	201.65	251.15	310.8	411.65
68.40	79.65	130.15	204.75	254.75	315.5	417.15
78.01				259.65		422.5
80.90	82.3	133.55	210.2	259.75	321.25	423.35
86.60	84.4	135.7	212.15	267.4	322.20	421.75
89.44				263.7		423.85
90.01	85.25	136.75	213.3	263.6	320.65	419.45
90.80				263.25		422.65
92.31				262.55		420.7
94.85	85.1	136.05	212.95	259.3	313.5	414.25
95.47				259.5		413.3
99.10	84.8	135.25	208.3	255.25	308.8	400.9
100.00	84.65	135.00	207.7	254.15	208.2	400.2

CALCULATION OF VAPOR COMPOSITION

The vapor phase composition was calculated by integration of the Gibbs-Duhem equation in the form

$$\ln \gamma_2 = -\frac{X_1}{X_2}\ln \gamma_1 + \int_0^{X_1} \frac{\ln \gamma_1}{X_2^2}\, dX_1 \qquad (1)$$

This equation, which assumes the liquid volume negligible compared to the vapor volume, was integrated numerically and solved simultaneously with the equation

$$P = P_1^0\Phi_1\gamma_1X_1 + P_2^0\Phi_2\gamma_2X_2 \qquad (2)$$

Φ is the ratio of the fugacity coefficients for the pure components to that in the mixture, both evaluated at the temperature and pressure of the mixture. Details of the numerical procedure are given elsewhere (*5*). The fugacity coefficients were estimated by the method of Prausnitz et al. (*13*). The fugacity correction was always small.

Vapor-liquid equilibria data are given in Tables V and VI (deposited with the ACS Microfilm Depository Service) and Figures 1 and 2. The numerical integration was carried out over increments of 0.025 mole fraction. The total pressures, reported to 0.01 mm of Hg, are interpolated values used in the integrations. The last digit in the pressure is not significant but is added to reduce error in computation. The first mole fraction given is 0.025 amine at which the vapor phase mole fractions are already quite high, 0.7 or above. For liquid mole fractions below 0.025 amine, the vapor phase composition can be calculated with good accuracy by assuming that water obeys Raoult's

Table IV. Results of Fitting Equilibrium Data to Equation

$$G^E/RT = AX(1 - X) + X(1 - X)(1 - 2X)[C_1 + C_2(1 - 2X) + C_3(1 - 2X)(1 - X)^6]$$

A	C_1	C_2	C_3	Av % error in G^E	Max error in G^E, cal/g-mol
		Triethylamine–water			
		5°C			
2.2405	0.15832	0.4455	0.7783	1.06	5.3
		10°C			
2.3232	0.17108	0.4681	0.8375	0.67	1.8
		15°C			
2.3933	0.18008	0.5346	0.9585	0.28	1.3
		18°C			
2.4178	0.20211	0.5681	0.9927	0.51	2.0
		Methyldiethylamine–water			
		10°C			
1.7983	0.01811	0.7496	0.1105	1.70	7.6
		20°C			
1.9409	0.08909	0.6312	0.5906	0.59	2.9
		30°C			
2.0656	0.15728	0.5597	0.8575	0.52	2.8
		35°C			
2.1477	0.20630	0.5351	0.8690	0.58	3.1
		40°C			
2.2067	0.24316	0.4808	0.8946	0.46	2.3
		47°C			
2.2647	0.27895	0.4527	0.9173	0.63	2.9

law since the activity coefficient for water is always less than 1.01 at this concentration, and the vapor phase is nearly ideal.

$$\therefore Y_a \doteq P - (P_w^0 X_w)/P \qquad (3)$$

Amine water solutions are extremely difficult to represent by the usual thermodynamically consistent polynomials. Copp and Everett (*3*) obtained a good fit for methyldiethylamine–water with an equation of the form

$$g^E/RT = A(T)X(1 - X) + \phi(X) \qquad (4)$$

$A = 2.176$ and 2.270 at 35° and 47°C, respectively, and

$$\phi(X) = X(1 - X)(1 - 2X)[0.250 + 0.460\ (1 - 2X) + 0.810\ (1 - 2X)(1 - X)^6] \qquad (5)$$

and X is the mole fraction of amine. This equation represents the excess free energy at 35° and 47°C to ±1 cal/mol, which is quite remarkable since ordinary polynomial expansions of several kinds give unsatisfactory results with six constants, and this equation has only four. Because of the success of Equations 4 and 5, the data for both triethylamine and methyldiethylamine–water were fitted with an equation of the same general form, and the results are given in Table IV.

Figures 3 and 4 show the calculated variation of g^E/T with $1/T$ and also furnish a check on the consistency of the results between temperatures. Some scatter does occur at high amine mole fractions at which the results are less accurate.

NOMENCLATURE

f = fugacity
g^E = excess Gibbs free energy, cal/g-mol
h^E = excess enthalpy, cal/g-mol
P = total pressure, mm of Hg
X = liquid phase mole fraction
Y = vapor phase mole fraction

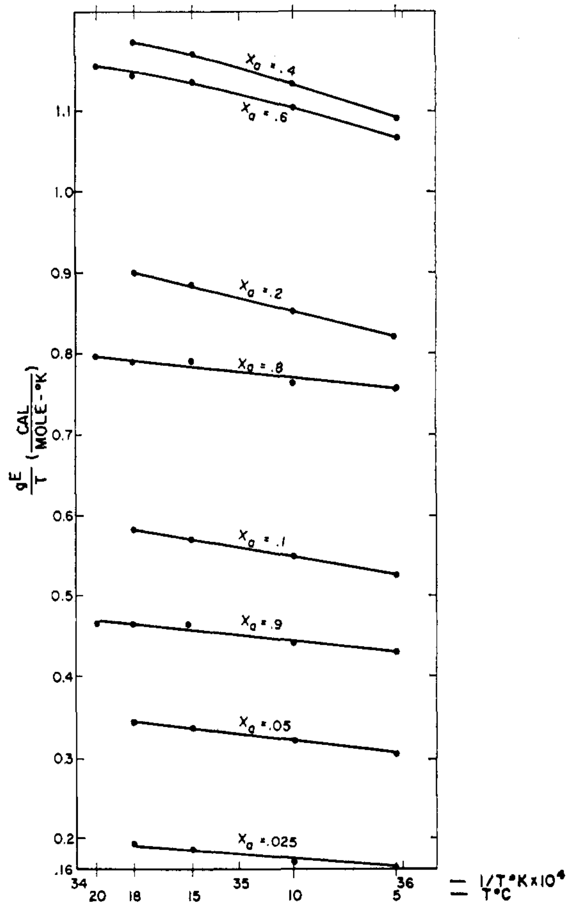

Figure 3. Excess Gibbs free energy for triethylamine–water

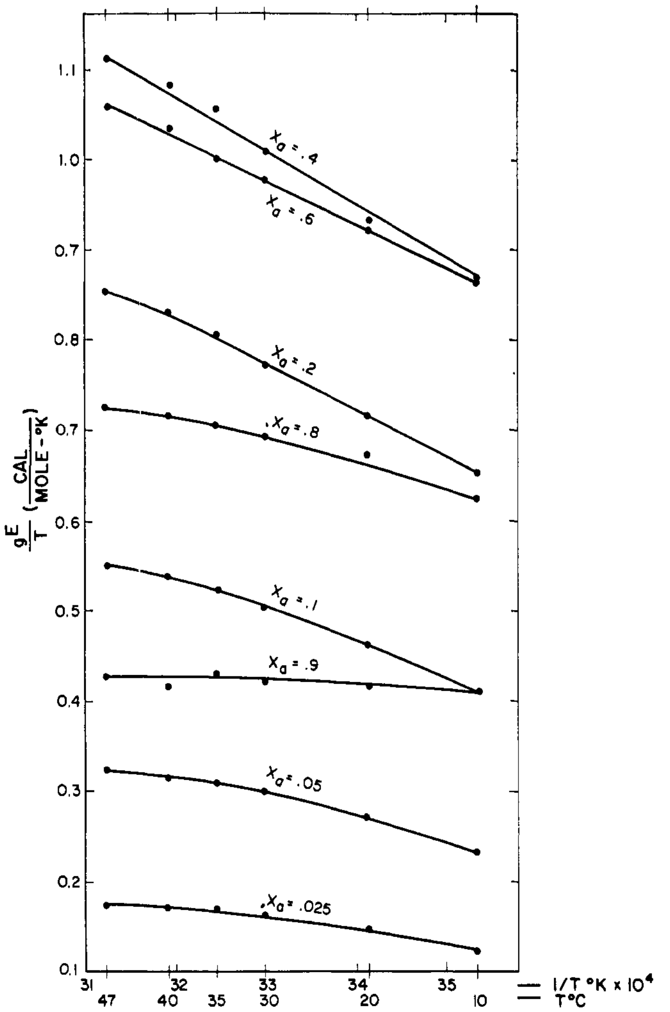

Figure 4. Excess Gibbs free energy for methyldiethylamine-water

Greek Letters

γ = activity coefficient = $f/f^0 X$
Φ = ratio of fugacity coefficient of pure component to component fugacity coefficient in mixture

Subscripts

a = amine
w = water
1 = Component 1
2 = Component 2

Superscript

0 = pure component

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RECEIVED for review August 14, 1970. Accepted June 28, 1971. Tables V (five manuscript pages, triethylamine–water) and VI (six manuscript pages, methyldiethylamine–water) will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order $4.00 for photocopy or $2.00 for microfiche.

Vapor-Liquid Equilibrium for System Toluene–*n*-Amyl Alcohol

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Total vapor pressures of mixtures of toluene and *n*-amyl alcohol were measured at temperatures from 30° C to the normal boiling point for liquid solutions of known compositions. These data were used to calculate isothermal vapor-liquid equilibrium compositions at five different temperatures from 30–110° C. The calculation procedure to convert the vapor pressure-temperature-liquid composition data to isothermal vapor-liquid equilibrium compositions is discussed.

CALCULATION METHODS

The approach outlined by Van Ness (*13*) was used to calculate the equilibrium compositions from the total vapor pressure data. The general coexistence equation is rigorous and derived from the Gibbs-Duhem equation. For a binary system, this equation is

$$\psi dP + \Omega dT = (y_1 - x_1) d \ln \left(\frac{\gamma_1^V}{\gamma_2^V}\right) + \frac{(y_1 - x_1)}{y_1(1 - y_1)}\, dy_1 \quad (1)$$

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