

r = signal from detector, V
 t = time, sec
 x = mole fraction volatile in liquid
 F = gas flow, cm³/sec
 H = Henry's law constant, (mol/cm³)_g/(mol/cm³)_l
 H' = proportionality constant, torr/(mol/cm³)_l
 P_v = vapor pressure of hydrocarbon, torr
 R = gas constant, 62361.0 torr-cm³/sec
 T = absolute temperature, K
 V = volume of volatile dissolved in liquid, cm³ vapor
 W = weight of stationary phase in column, g

Subscripts

a = argon
 A = average
 g = gas phase
 h = hydrocarbon
 i = inlet detector
 l = liquid phase
 o = outlet detector

Greek Letters

γ = activity coefficient
 ρ = density of stationary phase, g/cm³
 θ = upper time for integration, sec

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Vapor-Liquid Equilibrium of Methyl-*n*-Butylamine-Water

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Vapor-liquid equilibria are reported at 10°, 20°, 30°, and 40°C calculated by the total pressure method. Various thermodynamically consistent equations are examined for representing the results.

This work is part of a continuing study of hydrogen-bonding solutions involving amines, water, and alcohols. Previous work on various amine-water mixtures (1, 3) has shown them to be an interesting class with large excess functions, lower critical solution temperatures, where partial miscibility exists, and rather unusually shaped isothermal pressure-composition curves. In general, the excess free energy is poorly represented by the usual thermodynamically consistent polynomials and a large number of constants are necessary to obtain satisfactory agreement with the data.

Experimental

Total pressure-composition data were measured with a static apparatus that allows sample degassing without change in composition. Two samples can be run at once and pressures at up to six temperatures have been obtained in a day.

The apparatus consists of sample flasks, stopcocks, two manometers, and connecting glass tubing assembled on a frame with ball joints. The frame and apparatus, suspended in an aquarium water bath, can be rocked on its suspension to hasten equilibrium. The manometers are read through the plate glass with a cathetometer. Equilibrium, as indicated by steady pressure measurements, is usually reached in 10–15 min following stabilization of the temperature. When equilibrium has been obtained, the temperature may be increased and additional measurements obtained on the same samples. The apparatus and its operation have been completely de-

scribed (4). Temperatures were controlled to within 0.01°C by a thermistor-activated proportional controller. Temperatures were measured with a calibrated glass thermometer graduated in 0.1°C and the reported values are believed to be accurate within 0.03°C. Pressures were measured to within 0.05 mm of Hg. The accuracy of the measurements is probably within 0.1–0.2 mm, although leaks, failure to obtain equilibrium, or contamination by stopcock grease may occasionally cause greater errors. The largest pressure error that could result in the reported data from a temperature deviation of 0.03°C is about 0.2 mm of Hg at 40°C. The manometer readings were corrected for temperature and gravity. Vapor pressures of pure water were taken from Lange's Handbook (5).

The amine was distilled on a Stedman column at high reflux and a fraction boiling within 0.1°C was used. The fraction showed a single peak on a gas chromatograph.

Chemical analysis of the liquid phase was by acid titration of the amine, except above 90% amine by weight, where gas chromatography was employed. These methods gave amine concentrations within 1 part in 250 to 500. The low water concentrations are accurate to at least 1 mol %.

Calculation of Vapor-Liquid Equilibrium

Vapor compositions were not measured but were calculated by the total pressure method, in which pressure-liquid composition data are integrated with the Gibbs-Duhem equation. The latter was expressed in the form

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

By use of an integration formula, this equation was solved simultaneously at each increment with

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

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in which Φ is the ratio of the fugacity coefficient of the pure component to that of the same component in the mixture. Details of the numerical procedures have been given (3). The fugacity coefficients were evaluated using the method given by Prausnitz et al. (6) for low pressure vapor-liquid equilibrium.

Results

The experimental pressure-composition data are given in Table I. These results are also shown in Figure 1 along with vapor-liquid equilibrium compositions as calculated by the numerical integration (solid portion of curves) and by Raoult's law (dashed portion of curves). The first increment used in the integration was at a liquid mole fraction of 0.025, amine which, however, corresponded to vapor mole fractions of about 0.4 amine. The activity coefficient of the water was always below 1.01 at $x_a = 0.025$, and since the vapor pressure of water is lower than for amine, little error would result in assuming

$$y_a = \frac{p_a}{P} = \frac{P - p_w}{P} = \frac{P - P^{\circ}_w x_w}{P} \quad (3)$$

Table I. Experimental Pressure-Composition Results

Mole % amine	Pressures, mm of Hg			
	10°C	20°C	30°C	40°C
0.28	9.75	19.5	37.35	67.55
0.57	11.05	22.6	44.25	82.8
1.45	13.45	27.5	53.65	97.1
2.38	14.35	28.85	55.1	98.65
5.53	14.6	29.3	55.6	99.45
10.18	14.85	29.85	56.2	99.85
26.19	—	33.45	60.4	104.6
41.32	18.95	36.05	65.35	112.7
54.78	20.95	38.8	69.4	117.55
68.16	22.2	41.05	72.0	120.15
74.48	22.9	41.95	72.75	120.25
83.77	23.75	42.55	73.9	120.3
87.66	23.85	42.7	72.9	119.75
89.45	23.95	42.7	72.35	118.85
90.93	24.25	42.75	72.55	—
91.64	24.25	42.65	72.55	118.1
92.23	24.1	42.4	71.8	116.45
100.00	24.0	42.3	70.8	113.35

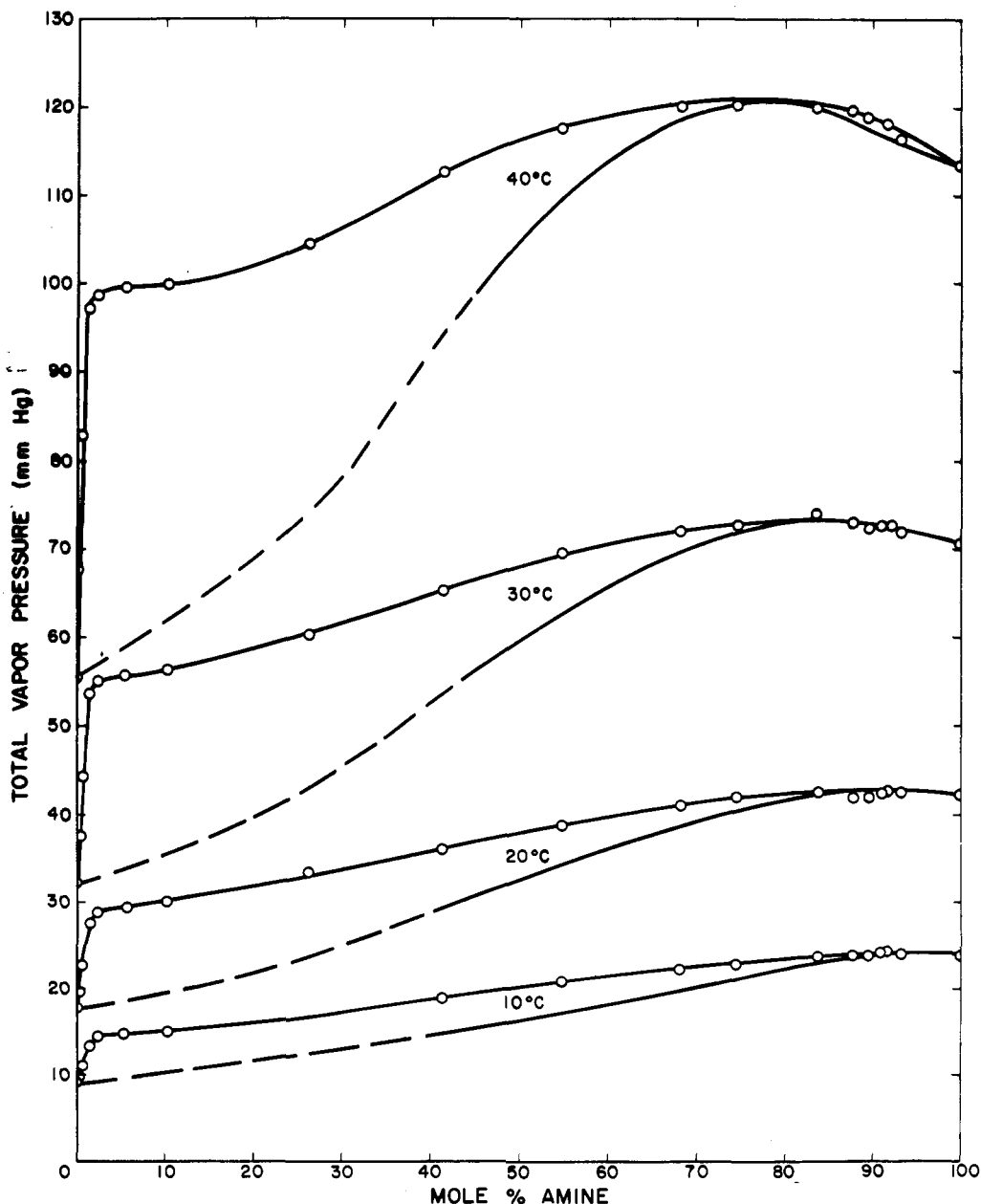
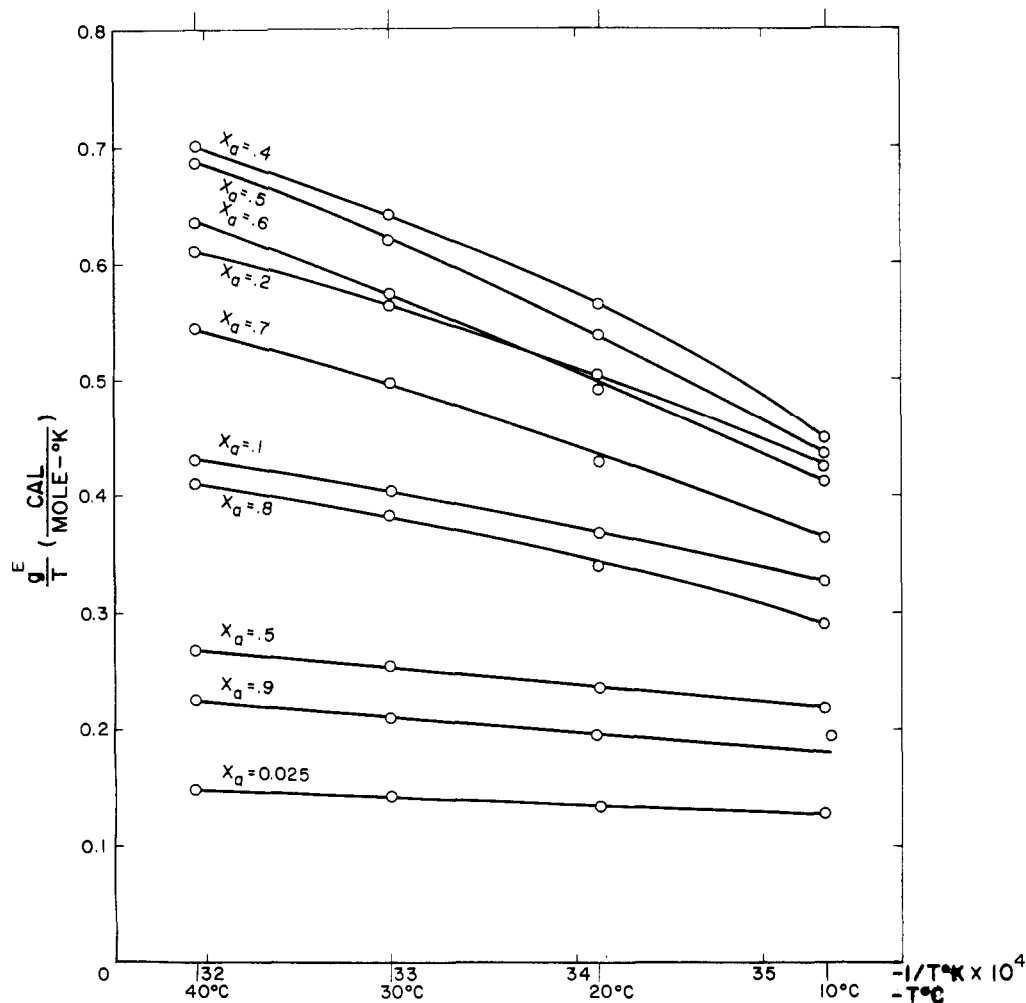


Figure 1. Pressure-composition data for methyl-n-butylamine-water

Figure 2. Excess Gibbs free energy for methyl-*n*-butylamine-water solutions vs. temperature



at lower amine concentrations.

Figure 2 shows plots of g^E/T vs. $1/T$ at various amine mole fractions. The excess free energies were calculated by the program. It is difficult to estimate the error in g^E , but judging from azeotrope mismatch and the effects of small pressure perturbations on the results of the numerical integration, the error should not exceed 2 or 3 cal/mol. The excess enthalpies at 25°C in Figure 3 were calculated from the slopes of the curves in Figure 2.

The total pressure curve for this system is interesting, in that there is such a rapid increase in pressure with increasing amine concentration in the dilute amine region. Of greater interest is the inflection that occurs at each temperature but is especially marked at 40°C. The existence of such behavior in azeotropic systems except at the critical solution point has been denied (7), though it is also exhibited by some other amine-water solutions. The lower critical solution temperature for the methyl-*n*-butylamine-water system is about 55°C.

The excess free energy and thus the activity coefficient of amine-water solutions have proved to be among the most difficult to represent by the usual thermodynamically consistent equations. The kind of equation used depends on its purpose: to represent the data as accurately as possible in compact form, or to develop parameters for use in a predictive scheme. If more than two or three constants are required to represent the results, it is almost certain that the constants will have no theoretical or predictive significance. In this event the simplest equation which will represent the data to the desired accuracy should be chosen. This does not necessarily mean the equation with the least number of arbitrary constants, since some higher order equations become complex.

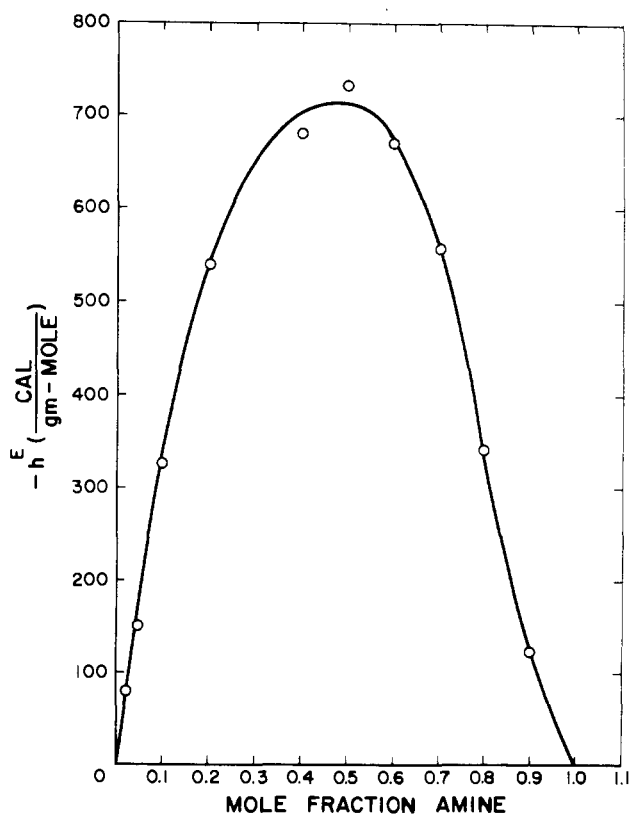


Figure 3. Excess enthalpies of mixing of methyl-*n*-butylamine-water at 25°C

In this work we investigated equations involving polynomial expansions of g^E/RTx_1x_2 and $\ln(\gamma_1/\gamma_2)$. The latter type was abandoned, since poorer results were obtained and a plot of these functions for this system shows the former to have less curvature than the latter.

Copp and Everett (2) found that an especially efficient function for representing the systems methyl-diethylamine-water and triethylamine-water was

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

$$\phi(x) = x(1-x)[A_0(1-2x) + A_1(1-2x)^2 + A_2(1-2x)^2(1-x)^6] \quad (4)$$

in which $A(T)$ was found at each temperature by dividing the value of g^E at $x = 0.5$ by $4RT$. This equation was applied to the methyl-*n*-butylamine-water data, but the representation was improved by letting the constants in $\phi(x)$ vary with temperature.

A study was also made of the power of the last term of the Copp and Everett equation and in general the sixth power was best, though at 40°C the third power gives a lower average error but greater maximum error.

The computed data for this system were also fitted by a simple power series of the form

$$g^E/RT = x_1x_2 \sum_{j=0}^n B_j x_1^j \quad (5)$$

in which component 1 is amine. This series is identical to the Redlich-Kister expansion but is somewhat easier to manipulate.

In any binary solution, the activity coefficients are related to the excess Gibbs free energy by

Table II. Relation Between Redlich-Kister Expansion, G^E/RTx_1x_2

$$= \sum_{j=0}^n C_j (x_1 - x_2)^j, \text{ and Power Series Expansion, } G^E/RTx_1x_2 = \sum_{j=0}^n B_j x_1^j$$

$$\begin{aligned} B_0 &= C_0 - C_1 + C_2 - C_3 + C_4 - C_5 \\ B_1 &= 2C_1 - 4C_2 + 6C_3 - 8C_4 + 10C_5 \\ B_2 &= 4C_2 - 12C_3 + 24C_4 - 40C_5 \\ B_3 &= 8C_3 - 32C_4 + 80C_5 \\ B_4 &= 16C_4 - 80C_5 \\ B_5 &= 32C_5 \\ C_0 &= B_0 + \frac{1}{2}B_1 + \frac{1}{4}B_2 + \frac{1}{8}B_3 + \frac{1}{16}B_4 + \frac{1}{32}B_5 \\ C_1 &= \frac{1}{2}B_1 + \frac{1}{2}B_2 + \frac{3}{8}B_3 + \frac{1}{4}B_4 + \frac{5}{32}B_5 \\ C_2 &= \frac{1}{4}B_2 + \frac{3}{8}B_3 + \frac{3}{8}B_4 + \frac{5}{16}B_5 \\ C_3 &= \frac{1}{8}B_3 + \frac{1}{4}B_4 + \frac{5}{16}B_5 \\ C_4 &= \frac{1}{16}B_4 + \frac{5}{32}B_5 \\ C_5 &= \frac{1}{32}B_5 \end{aligned}$$

Table III. Copp and Everett and Power Series Errors at 40°C

	Copp and Everett (2), 4 constants, "6th power"	$g^E/RTx_1x_2 = \sum_{j=0}^n B_j x_1^j$ Values of J					
		2	3	4	5	6	7
g^E cal/mol (av. error)	1.80	8.3	2.4	1.4	0.67	0.54	0.53
P mm (av. error)	0.75	3.2	1.3	0.76	0.43	0.39	0.36
P mm (max. error)	2.84	11.1	6.3	3.95	3.55	3.7	3.8

$$\ln \gamma = g^E/RT + (1-x) \frac{d(g^E/RT)}{dx} \quad (6)$$

Application of Equation 6 to Equation 5 yields

$$\ln \gamma_1 = x_2^2 \sum_{j=0}^n (J+1) B_j x_1^j \quad (7)$$

$$\ln \gamma_2 = x_1^2 \sum_{j=0}^{n-1} (J+1) (B_j - B_{j+1}) x_1^j + (n+1) B_n x_1^n \quad (8)$$

In the series for $\ln \gamma_1/x_2^2$ each constant involves only one constant from Equation 5 and in the expansion for $\ln \gamma_2/x_1^2$ each constant involves only two constants from Equation 5. The symmetry in the last expression is seen by writing out a few terms

$$\ln \gamma_2 = x_1^2 (B_0 - B_1) + 2(B_1 - B_2)x_1 + 3(B_2 - B_3)x_1^2 + 4(B_3 - B_4)x_1^3 + 5(B_4 - B_5)x_1^4 \quad (9)$$

Similarly, the corresponding expression for $\ln(\gamma_1/\gamma_2)$ involves two constants from Equation 5 per term as seen by

$$\ln(\gamma_1/\gamma_2) = B_0 - 2(B_0 - B_1)x_1 - 3(B_1 - B_2)x_1^2 - 4(B_2 - B_3)x_1^3 - 5(B_3 - B_4)x_1^4 \quad (10)$$

for a fourth-degree expansion. The relationship between these constants and those of the Redlich-Kister equation

$$g^E/RT = x_1x_2 \sum_{j=0}^n C_j (x_1 - x_2)^j \quad (11)$$

is given in Table II.

The comparison at 40°C of the Copp and Everett equations with various orders for the power expansion is given in Table III. The Copp and Everett equation represents g^E/RTx_1x_2 by an equation of ninth power but contains the same number of arbitrary constants as the third-order power series expansion. The higher order terms may well be helpful because of the very asymmetrical shape of the pressure curves which show two inflection points.

Even though Equation 4 is more efficient than Equation 5, it is also more complicated and by adding a few more constants Equation 5 becomes more accurate, as seen in Table III. For this reason we have given the results for the Copp and Everett and a sixth-order power expansion in Tables IV and V. It can be seen from Table III that the improvement is slow above sixth order.

The main argument for using Equation 5 is that it is possibly the simplest representation that can be used once two constants become inadequate.

Table IV. Constants for Copp and Everett Equation, $g^E/RTx_a x_w = A(T) + (1 - 2x_a)[A_0 + A_1(1 - 2x_a) + A_2(1 - 2x_a)(1 - x_a)^6]$

Temp., °C	A(T)	A ₀	A ₁	A ₂	Av. error		Max. error	
					g ^E , cal/mol	P, mm	g ^E , cal/mol	P, mm
10	0.87969	0.21137	0.53609	1.35154	0.84	0.083	2.84	0.29
20	1.08421	0.36991	0.49591	1.11018	0.91	0.17	2.89	0.75
30	1.25017	0.36725	0.41272	1.32658	1.54	0.38	3.30	1.33
40	1.38434	0.38405	0.34424	1.41676	1.80	0.75	4.89	2.84

Table V. Constants for Power Series Expansion, $g^E/RTx_a x_w = \sum_{j=0}^6 B_j x_a^j$

Temp	B ₀	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆
10	2.9747	-15.7074	53.9486	-103.0110	107.0518	-54.3339	10.2936
20	3.1353	-15.7621	63.0520	-150.9256	202.8192	138.6671	37.4737
30	3.3024	-14.7264	54.3636	-124.0346	163.6898	-111.2495	29.7642
40	3.3871	+13.2271	43.1249	-88.6044	109.8023	-72.4448	19.1432

Temp. °C	Av. error		Max. error	
	g ^E , cal/mol	P, mm	g ^E , cal/mol	P, mm
10	1.02	0.11	2.10	0.30
20	0.33	0.07	0.71	0.72
30	0.44	0.19	1.19	1.67
40	0.54	0.39	1.9	3.7

Nomenclature

A, B, C, = constants in the expansions of g^E
 g^E = excess Gibbs free energy, cal/mole
 h^E = excess enthalpy, cal/mole
P = total pressure, mm of Hg
 P° = vapor pressure of pure component, mm of Hg
p = partial pressure, mm of Hg
x = mole fraction in liquid
y = mole fraction in vapor

Greek Letters

γ = activity coefficient
 ϕ = ratio of fugacity coefficients

Subscripts

a = amine
w = water

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