Vapor-Liquid Equilibrium of *N*-Ethyl-*n*-Butylamine–Water and *N*-Ethyl-*sec*-Butylamine–Water

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The vapor-liquid equilibria of *N*-ethyl-*n*-butylamine–water are reported at 10°, 20°, 30°, and 39.95° C., and of *N*-ethyl-*sec*-butylamine–water at 10°, 15°, 20°, 25°, 30°, and 39.95° C.

THIS WORK is part of a continuing study of phase relations in highly nonideal hydrogen bonding-type solutions. Amines and water are among the examples in this category, with large values for all the excess functions having lower critical solution points and solubility curves that are very temperature-sensitive, and exhibiting excess free energies that are extremely difficult to represent by the usual thermodynamically consistent polynomials.

EXPERIMENTAL

The apparatus and the experimental methods used in this work have been described (*1, 2*). In brief, the apparatus is a static vapor pressure device in which a mixture can be degassed without change in composition. The entire apparatus, consisting of sample flasks, mercury manometers, and glass manifold, is submerged in a constant-temperature bath and suspended so that it can be agitated to hasten equilibrium.

The manometers are read within the bath by means of a cathetometer to 0.05 mm. of Hg. The reproducibility of the pressure measurements is indicated in Tables I and II by the pressures corresponding to two liquid phases. In each column, these values should be identical, since two phases are present. The *N*-ethyl-*n*-butylamine data agree within 0.2 mm. of Hg, and the *N*-ethyl-*sec*-butylamine data agree within 0.1 mm. of Hg, except for one value.

Since none of the total vapor pressures exceeded the length of the submerged manometers (about 130 mm.), a high vacuum was maintained on the external manometer leg, and the vapor pressure was determined from the manometer reading and the temperature correction. The correction for the density of the vapor leg was insignificant.

Table I. Experimental Vapor Pressure of *N*-Ethyl-*n*-butylamine–Water Mixtures

Mole % Amine	Temp., ° C. 10	20	30	39.95
	Pressure, Mm. of Hg			
0.320	10.15	20.8	40.85	78.85
0.627	11.5	24.4	49.15	88.55^a
4.44	13.35^a	26.9^a	50.2^a	88.65^a
15.4	13.4	26.75^a	50.25^a	88.75^a
29.6	13.85	26.95	50.1^a	88.7^a
40.8	13.9	27.1	50.3	88.45
49.2	13.95	27.0	50.15	88.3
58.5	13.65	26.65	49.5	87.0
69.0	13.35	25.95	48.05	84.6
79.5	12.85	24.65	45.55	79.8
86.3	12.2	23.5	42.95	74.85
89.3	11.7	22.3	40.8	70.6
94.9	10.9	20.5	36.75	62.55
100.0	9.7	17.95	31.35	52.05

^{a} Two liquid phases.

Table II. Experimental Vapor Pressures of *N*-Ethyl-sec-butylamine–Water Mixtures

Mole % Amine	Temp., ° C. 10	15	20	25	30	39.95
	Pressure, Mm. of Hg					
0.393	10.95	16.0	23.45	33.6	47.75	91.2
0.568	12.05	17.75	26.15	37.95	54.25	104.4
1.658	16.75	24.85	36.1	50.85^a	69.25^a	120.8^a
3.44	17.95	25.85	36.7	50.85^a	69.25^a	120.8^a
6.84	18.25	26.1	36.85	50.85^a	69.3^a	...
14.66	18.70	26.45	37.05	50.85^a	69.2^a	...
25.5	19.65	27.45	37.85	51.55	69.35	120.8^a
35.8	20.5	28.35	39.1	52.65	70.4	121.0^a
47.4	21.15	29.25	39.85	53.6	71.45	121.8
60.5	21.7	29.9	40.5	54.2	72.05	122.25
72.4	21.95	29.9	40.5	54.1	71.65	121.05
78.4	21.95	29.85	40.4	53.75	71.1	119.55
85.6	21.7	29.4	29.65	52.65	69.25	116.15
91.5	21.3	28.7	38.5	50.95	66.75	110.7
94.8	20.80	27.95	37.25	49.2	64.1	105.4
100.00	19.2	25.5	33.5	43.5	56.0	89.55

^{a} Two liquid phases.

The temperature was controlled to within 0.01° C. by a thermistor-operated Sargent temperature controller. An external circulating pump maintained a uniform temperature within the bath. The temperature was measured with an accuracy of about 0.03° C. with a calibrated glass thermometer graduated in tenths of a degree. This would result in a maximum pressure error of less than 0.2 mm. of Hg.

Pure *N*-ethyl-*n*-butylamine was prepared from the commercial product by distillation on a Stedman column. Fractions having a boiling range of 0.1° C. were used. *N*-ethyl-*sec*-butylamine was synthesized for this work and was of similar purity. All fractions used showed a single peak on the gas chromatograph described below.

Chemical analysis of the liquid phase was by acid titration of the amine, except at water concentrations below about 10 wt. %. At low water content, analysis was by gas chromatography, using a 20-foot by ¼-inch column packed with Flouropac (Aerograph) with a silicone coating. These methods gave amine concentration reproducibilities of one part in 250 to 500, and water concentrations having a maximum deviation of ±1 mole %.

Water vapor pressures were taken from Lange's Handbook (*3*). These data agree very closely with the correlating equations used in calculating the 1967 ASME steam tables over the temperature range in question.

The heterogeneous liquid phase compositions (Table III) were obtained by two methods. The amine-rich phases were determined by cloud points. Various solution concen-

Table III. Liquid-Liquid Phase Equilibria for *N*-Ethyl-*n*-butylamine and *N*-Ethyl-sec-butylamine with Water

Temp., ° C.	Mole Fraction Amine	
	Water-rich phase	Amine-rich phase
	N-Ethyl-*n*-butylamine	
10	0.0201	0.0885
20	0.0101	0.162
30	0.0071	0.303
40	0.0053	0.380
	N-Ethyl-*sec*-butylamine	
25	0.0160	0.177
30	0.0117	0.257
40	0.0079	0.407

trations were made by weight, sealed in glass tubes, and totally immersed in a water bath. The temperature was slowly increased, and the cloud points were observed. These data were plotted, and the values in Table III were interpolated from the curve. The water-rich phase compositions were obtained by acid titration of samples withdrawn from heterogeneous solutions equilibrated at the desired temperatures.

The accuracy of the amine content of the water-rich phase is at least 1 part in 250. That of the amine-rich phase is less predictable. Seven cloud points between 22° and 44° C. were determined for ethyl-*sec*-butylamine, and seven between 9° and 50° C. were measured for ethyl-*n*-butylamine. Though the points formed smooth curves, interpolation could result in errors as large as 1 mole %.

CALCULATION OF THE VAPOR COMPOSITION

Vapor compositions cannot be measured with this apparatus, but they can be calculated by the total pressure method, in which the Gibbs-Duhem equation is integrated with the total pressure–liquid composition data.

Two computer programs were used to integrate the total pressure–liquid composition data, and these have been described previously (*2*).

In one, the Gibbs-Duhem equation is expressed in the form

$$\Delta p_2 = \frac{\Delta P}{1 - \dfrac{p_1 x_1}{p_2 x_2}} \tag{1}$$

in which the p and P are partial and total pressures, respectively, and x is the liquid composition. The subscripts refer to components 1 and 2.

The second program integrates the Gibbs-Duhem equation in the form

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

This equation is solved simultaneously at each increment of concentration with the equation

$$P = p_1^\circ x_1\gamma_1 + p_2^\circ x_2\gamma_2 \tag{3}$$

in which γ is the activity coefficient defined by $p/p^\circ x$, and the superscript refers to a pure component. Both Equations 1 and 2 become indeterminate at the azeotrope, and so the integration must proceed from each pure component to the azeotrope.

In both programs, the gas phase was assumed to be ideal. At these temperatures, the second virial coefficient of water is about −1000 cm.^{3} per gram-mole. Those of the amines are not available, but the isomer triethylamine has a value of about −1600 cm.^{3} per gram-mole. At the very low pressures involved, neglecting vapor phase nonideality will result in an error of not over 1 part per 100 in the vapor mole fractions.

The data in Tables IV and V (complete tables deposited with ASIS/NAPS) come from both programs and were chosen according to smoothness and goodness of fit at the azeotrope. The program using Equations 2 and 3 has the capability of integrating across the immiscible regions (Table III), so it was always used on the part of the curve containing the immiscible region for systems having homogeneous azeotropes. The remainder of Table IV and Table V, which include all the other temperatures for both systems, have been deposited with the ASIS National Auxiliary Publications Service.

The data in Tables I and II were plotted, and values of pressure for intervals of 0.025 mole fraction were read from the curve. These pressures are given to 0.01 mm. of Hg to reduce computer error. The measured pressures, Tables I and II, were only determined to 0.05 mm. of Hg. In general, these curves passed directly through the data points. In several instances, points were as much as 0.1 mm. of Hg from the curve. The maximum deviation was 0.3 mm. for 86.3 mole % *N*-ethyl-*n*-butylamine at 20°, 30°, and 39.95° C.

The interpolated pressure values and the solubility data were fed to the computer. The numerical integrations were carried out over these increments, except near a heterogeneous region. Here the increment was adjusted to terminate or begin exactly at the solubility. The input pressures and compositions, and the output vapor compositions, activity coefficients, and excess free energies are given in Tables IV and V.

Because of the low solubility of the amine in the water-rich phase, vapor compositions in heterogeneous regions may be calculated by assuming that water obeys Raoult's law. For instance, at 20° C. the solubility of *N*-ethyl-*n*-butylamine in water is 1%. Assuming that water obeys Raoult's law, its partial pressure is 99% of the vapor pressure of water at 20° C., or 17.36 mm. of Hg. The mole fraction of amine, then, is given by $(P - p_w)/P$, or $(26.85 - 17.36)/26.85 = 0.353$.

Table IV. Calculated Vapor-Liquid Equilibria of *N*-Ethyl-sec-butylamine–Water at 20° C.[a]

x_a	y_a	γ_a	γ_w	G^E	P
0.0					17.54
0.025	0.533	23.274	. . .	45.8	36.65
0.05	0.536	11.738	1.026	86.1	36.82
0.10	0.538	5.934	1.082	145.1	36.97
0.15	0.540	3.980	1.146	187.8	37.10
0.20	0.545	3.040	1.214	219.7	37.40
0.25	0.553	2.496	1.285	242.7	37.83
0.30	0.566	2.166	1.358	259.6	38.44
0.35	0.579	1.925	1.438	270.9	38.97
0.40	0.592	1.740	1.530	277.4	39.40
0.45	0.603	1.587	1.636	278.7	39.72
0.50	0.616	1.471	1.755	276.1	40.03
0.55	0.629	1.373	1.896	269.2	40.27
0.60	0.644	1.297	2.050	258.0	40.46
0.65	0.662	1.232	2.236	242.9	40.56
0.70	0.700	1.211	2.316	224.8	40.58
0.75	0.716	1.154	2.624	202.8	40.51
0.80	0.733	1.102	2.066	175.6	40.29
0.85	0.763	1.065	3.578	142.6	39.75
0.90	0.800	1.032	4.457	103.3	38.90
0.95	0.862	1.007	5.818	55.1	37.17
1.00					33.50

[a] Complete table deposited with ASIS/NAPS.

It is very difficult to represent the equilibria for these systems by the usual thermodynamically consistent polynomials. By truncating the data at a mole fraction amine of 0.6 (89.4 wt. %) and using a large number of constants, a good fit was obtained in some cases.

The data in Table IV were fitted with a 6-constant Chebyshev polynomial. The function fitted was $\ln\gamma_a/x_w^2$. The 13 pressure points in Table IV from 0.025 to 0.6 were represented with an average error of 0.3 mm. and a maximum error of 1.2 mm. at a mole fraction of 0.05. A Chebyshev fit tends to minimize the maximum error. Even so, a considerable error always occurs at low amine mole fractions.

The polynomial for ethyl-*sec*-butylamine at 20° C. in terms of mole fraction amine is

$$\frac{\ln\gamma_a}{x_w^2} = 3.9500 - 30.469x_a + 168.51x_a^2 - 478.89x_a^3 + 668.08x_a^4 - 358.15x_a^5$$

NOMENCLATURE

G^E = excess Gibbs free energy in cal. per gram-mole
P = total pressure in mm. of Hg
p = partial pressure in mm. of Hg
x = mole fraction in the liquid
y = mole fraction in the vapor

Greek

γ = activity coefficient, $p/p^\circ x$

Subscripts

1 = component 1
2 = component 2
w = water
a = amine

Superscripts

o = pure component

LITERATURE CITED

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Vapor-Liquid Equilibria of Binary Systems of Water with Methanol and Ethanol at Extreme Dilution of the Alcohols

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A new method for determining vapor-liquid equilibrium data for binary systems, including measurements at concentrations of one of the components in the parts per million range, is described. The method is based on the use of radioactive tracers, as the component in low concentration is added partly in an isotopic form. The method has been tried at 760 mm. of Hg pressure for two systems, methanol-water and ethanol-water, at low concentrations of the alcohols. Separation factors and activity coefficients for the alcohols at extreme dilution are given. The data have been tested for thermodynamic consistency and proved consistent.

THE DEMAND for very pure chemicals has made extractive distillation, with a high grade of purification ability, an often-used separation operation. This means that experimentally verified values of separation factors, the K-values, at extreme dilution would be very useful.

Vapor-liquid equilibrium investigations reported in the literature have seldom been performed at concentrations of any of the components lower than 0.5 mole %, mostly because the available and reproducible methods of analysis such as density, index of refraction, etc., do not allow accurate determinations of concentrations lower than this limit.

This investigation presents a method for determining separation factors at very low concentrations of one of the components, using radioactive labeled compounds as tracers. The use of isotopic tracers makes it possible to measure very small amounts of the component in question.

This novel method has been used for the binary systems of water with methanol and ethanol at very low concentrations of the alcohols.

EXPERIMENTAL

Apparatus. A slightly modified equilibrium still modeled on the principle of Thornton (*3*) was used. The most important modification was the introduction of a cooling facility of the condensate trap to prevent the condensate, the boiling point of which is up to 10° C. lower than that of the liquid, from boiling and fractionizing.

Figure 1 shows the still, the working principle of which is well known. The temperature inside the cylinder surrounding the two traps, the Cottrell tube, and the disengagement chamber, is kept constantly about 1° C. above the boiling point that is measured in the disengagement chamber. The temperature in the vapor line is kept about 5° C. higher than the boiling point.

The temperatures are measured with thermistors and recorded on a strip chart recorder. The accuracy of the temperature measurements were ±0.02° C.

All the experiments are run at 760 mm. of Hg pressure, kept constant within ±1 mm. of Hg with a mercury-