Vapor-Liquid Equilibria of Water-Diisopropylamine and Water–Di-*n*-Propylamine

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The vapor-liquid equilibria of diisopropylamine-water and di-*n*-propylamine–water solutions are reported. Data are given at 10°, 15°, 20°, 25°, 30°, and 39.95° C. for diisopropylamine and at 10°, 20°, 30°, and 39.95° C. for di-*n*-propylamine.

WATER VAPOR PRESSURES were taken from Lange's handbook (*5*). Between 10° and 40° C. the values given by Lange never differ by more than 0.01 mm. of Hg from values derived from the correlating equations used in calculating the 1967 ASME steam tables.

EXPERIMENTAL

The vapor pressures of the pure amines and of amine-water mixtures were measured with a static apparatus described previously (*3*), which employs especially designed flasks that permit the liquid samples to be degassed without change in composition. These flasks are connected to mercury manometers, and the entire assembly is suspended in the constant temperature bath and may be agitated to hasten equilibrium.

Total pressure measurements were made using a cathetometer to read the manometers in the bath. If the pressure exceeded the range of the manometer, a back-pressure was provided by water in another flask immersed in the same bath. The manometer readings were corrected for temperature. The accuracy of the pressure measurements was about 0.1 mm. of Hg. Temperatures were measured with a calibrated glass thermometer and have an accuracy within 0.03° C. A thermistor-operated Sargent temperature controller and an external circulating pump maintained the temperature within about 0.01° C.

The liquid phase was analyzed by acid titration when the water concentration was greater than 10% by weight. For lower concentrations, a gas chromatograph was used with a 20-foot by 1/4-inch column packed with Fluoropac coated with 10% GE·SF-96 Silicone (Aerograph). At 150° F. and a helium flow of 30 ml. per minute the retention times were 2½ to 3 minutes for water and about 6 minutes for the amines. These methods gave amine concentration reproducibilities to 1 part in 250 to 500, and water concentrations having a maximum deviation of 1 mole %.

The liquid-phase compositions of the partially miscible solutions (Table I) were obtained by two methods. The diisopropylamine data and the water-rich phase data for di-*n*-propylamine were obtained by acid titration of the equilibrated phases. The amine-rich phase for di-*n*-propylamine was determined from cloud points. Various solutions were made by weight and sealed in glass tubes. These tubes were immersed completely in a water bath, the temperature was slowly increased, and the cloud points were observed. These data were plotted and the values in Table I were interpolated from the curve.

Table I. Liquid-Liquid Phase Equilibrium for Diisopropylamine and Di-*n*-propylamine

Temp., ° C.	Mole Fraction Amine Water-rich phase	Mole Fraction Amine Amine-rich phase
	(Diisopropylamine)	
30	0.0211	0.2155
40	0.0126	0.408
	(Di-*n*-propylamine)	
10	0.01389	0.269
20	0.00902	0.336
30	0.00677	0.425
40	0.00498	0.498

CALCULATION OF VAPOR COMPOSITION

The vapor composition cannot be measured directly with the apparatus used. However, since the vapor analysis is

Table II. Experimental Vapor Pressures of Diisopropylamine-Water Mixtures

	Temperature, ° C.					
Mole % Amine	10	15	20	25	30	39.95
	Pressure, Mm. Hg					
0.379	11.95	17.7	25.85	37.45	53.5	103.65
0.632	14.0	21.25	30.95	46.5	67.2	131.5
1.40	19.85	30.4	46.0	67.55	96.7	...
2.49	25.4	37.2	53.55	75.25	103.2^a	...
4.30	27.2	38.85	54.95	76.0	103.1^a	...
9.99	28.55	40.15	55.9	76.4	103.1^a	...
24.3	31.15	42.8	58.4	78.05	103.65	175.9^a
36.5	33.4	45.2	60.9	80.55	105.8	175.9^a
57.4	36.3	48.5	64.35	84.45	109.85	178.85
70.3	37.8	50.15	66.15	86.3	111.55	180.55
79.8	38.5	50.75	66.8	86.8	112.2	180.8
85.2	38.7	51.0	66.85	86.7	111.9	179.45
87.2	38.8	51.15	67.15	86.75	111.45	178.2
94.6	38.65	50.65	65.95	84.75	108.0	169.75
100.0	37.9	49.25	63.5	80.75	102.35	157.75

^{a} 2 liquid phases.

Table III. Experimental Vapor Pressures of Di-*n*-Propylamine–Water Mixtures

	Temperature, ° C.			
Mole % Amine	10	20	30	39.95
	Pressure, Mm. Hg			
0.308	10.45	21.8	43.45	81.8
0.489	11.2	24.2	49.75	95.2
^{a}	15.15^a	29.9 ^{a}	55.45^a	96.95^a
40.2	15.4	29.95	55.5 ^{a}	97.0 ^{a}
47.6	15.35	29.95	53.35	97.0 ^{a}
63.3	15.25	29.6	54.55	95.55
78.3	14.65	28.2	51.7	90.5
85.2	13.7	26.4	48.75	85.05
85.85	13.95	26.5	48.5	84.45
93.1	13.1	24.65	44.55	76.15
94.6	12.45	23.6	42.25	72.3
100.0	11.0	20.1	34.75	57.6

^{a} 2 liquid phases.

Table IV. Calculated Vapor-Liquid Equilibria of Diisopropylamine-Water

x	y	γ_1	γ_2	G^E	P	x	y	γ_1	γ_2	G^E	P
		At 10° C.						At 25° C.			
0					9.21	0					23.76
0.05	0.672	9.709	1.029	79.1	27.40	0.05	0.696	13.094	1.026	90.7	76.06
0.10	0.686	5.169	1.081	131.6	28.55	0.10	0.697	6.589	1.083	154.4	76.40
0.15	0.698	3.612	1.137	169.5	29.43	0.15	0.699	4.428	1.146	200.5	76.76
0.20	0.710	2.842	1.195	197.8	30.35	0.20	0.701	3.359	1.215	235.6	77.33
0.25	0.722	2.386	1.257	218.9	31.29	0.25	0.706	2.734	1.290	261.9	78.17
0.30	0.735	2.084	1.323	234.2	32.23	0.30	0.712	2.326	1.372	280.9	79.16
0.35	0.748	1.869	1.395	244.7	33.14	0.35	0.719	2.041	1.462	293.9	80.24
0.40	0.760	1.703	1.474	250.8	33.97	0.40	0.726	1.828	1.562	301.3	81.32
0.45	0.771	1.569	1.567	252.9	34.69	0.45	0.734	1.662	1.677	303.7	82.30
0.50	0.782	1.460	1.672	251.0	35.37	0.50	0.741	1.528	1.811	301.4	83.20
0.55	0.794	1.370	1.794	245.3	36.00	0.55	0.750	1.418	1.968	294.4	84.03
0.60	0.806	1.298	1.930	236.0	36.63	0.60	0.759	1.330	2.150	282.7	84.87
0.65	0.819	1.238	2.089	223.1	37.24	0.65	0.770	1.256	2.365	266.3	85.63
0.70	0.832	1.185	2.291	206.6	37.76	0.70	0.782	1.193	2.641	245.6	86.26
0.75	0.846	1.136	2.560	186.0	38.19	0.75	0.792	1.132	3.039	219.8	86.63
0.80	0.860	1.092	2.937	160.8	38.52	0.80	0.802	1.078	3.611	187.8	86.80
0.85	0.875	1.052	3.514	130.0	38.73	0.85	0.840	1.061	3.910	150.7	86.71
0.90	0.894	1.017	4.466	92.6	38.80	0.90	0.868	1.029	4.769	107.8	86.15
0.95	0.942	1.010	4.870	50.0	38.62	0.95	0.914	1.007	6.106	57.2	84.48
1.00					37.90	1.00					80.75
		At 15° C.						At 30° C.			
0					12.79	0					31.82
0.05	0.681	10.801	1.025	81.4	39.02	0.05		Heterogeneous			103.10
0.10	0.691	5.627	1.078	137.7	40.15	0.10		Heterogeneous			103.10
0.15	0.699	3.880	1.137	178.9	41.03	0.15		Heterogeneous			103.10
0.20	0.708	3.016	1.199	209.7	41.98	0.20		Heterogeneous			103.10
0.25	0.718	2.505	1.266	232.6	42.98	0.25	0.701	2.841	1.301	276.0	103.75
0.30	0.729	2.166	1.337	249.2	43.98	0.30	0.705	2.403	1.386	296.0	104.65
0.35	0.738	1.926	1.416	260.8	44.97	0.35	0.710	2.091	1.482	309.4	105.55
0.40	0.748	1.741	1.506	267.5	45.84	0.40	0.715	1.860	1.590	316.9	106.50
0.45	0.758	1.597	1.607	269.9	46.68	0.45	0.722	1.685	1.710	319.0	107.52
0.50	0.768	1.479	1.722	267.5	47.44	0.50	0.729	1.546	1.848	316.1	108.53
0.55	0.778	1.383	1.856	261.4	48.16	0.55	0.737	1.433	2.009	308.3	109.47
0.60	0.789	1.305	2.010	251.2	48.86	0.60	0.745	1.337	2.207	295.7	110.22
0.65	0.802	1.240	2.194	237.3	49.51	0.65	0.755	1.258	2.443	278.2	110.92
0.70	0.814	1.182	2.427	219.2	50.07	0.70	0.766	1.192	2.734	255.7	111.50
0.75	0.826	1.129	2.744	196.6	50.50	0.75	0.781	1.140	3.076	228.2	111.96
0.80	0.839	1.082	3.195	169.1	50.81	0.80	0.805	1.103	3.436	195.9	112.20
0.85	0.855	1.042	3.844	135.6	51.00	0.85	0.818	1.052	4.270	157.1	111.90
0.90	0.895	1.030	4.188	97.0	51.02	0.90	0.851	1.022	5.170	110.8	110.60
0.95	0.934	1.010	5.203	52.5	50.58	0.95	0.909	1.005	6.195	57.9	107.60
1.00					49.25	1.00					102.35
		At 20° C.						At 39.95° C.			
0					17.54	0					55.15
0.05	0.690	11.947	1.025	86.0	55.07	0.05		Heterogeneous			175.9
0.10	0.695	6.117	1.080	145.9	55.90	0.10		Heterogeneous			175.9
0.15	0.700	4.161	1.141	189.7	56.66	0.15		Heterogeneous			175.9
0.20	0.706	3.199	1.206	222.7	57.55	0.20		Heterogeneous			175.9
0.25	0.713	2.629	1.276	247.7	58.53	0.25		Heterogeneous			175.9
0.30	0.721	2.255	1.353	265.3	59.57	0.30		Heterogeneous			175.9
0.35	0.729	1.987	1.440	277.8	60.57	0.35		Heterogeneous			175.9
0.40	0.738	1.787	1.535	285.0	61.55	0.40		Heterogeneous			175.9
0.45	0.746	1.629	1.644	286.9	62.42	0.45	0.694	1.727	1.782	350.6	176.69
0.50	0.754	1.501	1.772	284.9	63.21	0.50	0.699	1.574	1.939	346.9	177.61
0.55	0.763	1.398	1.920	278.2	63.97	0.55	0.705	1.450	2.123	337.7	178.47
0.60	0.774	1.314	2.088	266.8	64.72	0.60	0.712	1.348	2.344	323.1	179.25
0.65	0.785	1.244	2.292	251.7	65.43	0.65	0.720	1.263	2.610	303.3	179.92
0.70	0.799	1.187	2.532	232.3	66.10	0.70	0.733	1.199	2.910	278.1	180.51
0.75	0.812	1.135	2.857	208.0	66.59	0.75	0.757	1.157	3.189	248.3	180.87
0.80	0.820	1.079	3.419	178.4	66.80	0.80	0.761	1.090	3.913	212.7	180.76
0.85	0.825	1.056	3.738	142.1	66.82	0.85	0.783	1.047	4.712	168.9	179.37
0.90	0.888	1.034	4.280	102.3	66.60	0.90	0.824	1.020	5.601	118.1	175.69
0.95	0.923	1.007	5.761	54.9	65.82	0.95	0.890	1.003	6.761	60.8	168.90
1.00					63.50	1.00					157.75

Table V. Calculated Vapor-Liquid Equilibria of Di-*n*-Propylamine–Water

x	y	γ_1	γ_2	G^E	P	x	y	γ_1	γ_2	G^E	P
		At 10° C.						At 30° C.			
0					9.21	0					31.82
0.05		Heterogeneous			15.16	0.05		Heterogeneous			55.50
0.10		Heterogeneous			15.16	0.10		Heterogeneous			55.50
0.15		Heterogeneous			15.16	0.15		Heterogeneous			55.50
0.20		Heterogeneous			15.16	0.20		Heterogeneous			55.50
0.25		Heterogeneous			15.16	0.25		Heterogeneous			55.50
0.30	0.409	1.886	1.395	283.2	15.22	0.30		Heterogeneous			55.50
0.35	0.429	1.709	1.463	244.6	15.34	0.35		Heterogeneous			55.50
0.40	0.445	1.557	1.547	246.8	15.40	0.40		Heterogeneous			55.50
0.45	0.472	1.475	1.610	245.5	15.46	0.45	0.439	1.554	1.778	310.1	55.43
0.50	0.489	1.373	1.712	240.2	15.44	0.50	0.464	1.474	1.864	304.2	55.27
0.55	0.513	1.306	1.812	232.9	15.40	0.55	0.480	1.384	1.997	294.9	55.04
0.60	0.535	1.241	1.938	221.6	15.32	0.60	0.495	1.298	2.174	281.3	54.74
0.65	0.560	1.190	2.075	207.2	15.19	0.65	0.509	1.224	2.396	263.1	54.33
0.70	0.586	1.143	2.254	189.7	15.02	0.70	0.527	1.162	2.660	240.1	53.68
0.75	0.612	1.098	2.496	168.1	14.80	0.75	0.553	1.116	2.959	212.7	52.62
0.80	0.646	1.063	2.783	142.4	14.47	0.80	0.586	1.079	3.311	180.8	51.05
0.85	0.688	1.032	3.174	112.5	14.03	0.85	0.634	1.049	3.755	144.1	48.90
0.90	0.753	1.013	3.576	78.3	13.32	0.90	0.692	1.021	4.481	101.7	46.20
0.95	0.849	1.002	4.044	40.3	12.33	0.95	0.791	1.003	5.503	52.8	41.85
1.00					11.00	1.00					34.75
		At 20° C.						At 39.95° C.			
0					17.54	0					55.15
0.05		Heterogeneous			29.90	0.05		Heterogeneous			97.0
0.10		Heterogeneous			29.90	0.10		Heterogeneous			97.0
0.15		Heterogeneous			29.90	0.15		Heterogeneous			97.0
0.20		Heterogeneous			29.90	0.20		Heterogeneous			97.0
0.25		Heterogeneous			29.90	0.25		Heterogeneous			97.0
0.30		Heterogeneous			29.90	0.30		Heterogeneous			97.0
0.35	0.421	1.790	1.520	277.1	29.92	0.35		Heterogeneous			97.0
0.40	0.426	1.586	1.635	279.0	29.95	0.40		Heterogeneous			97.0
0.45	0.439	1.453	1.743	275.8	29.96	0.45		Heterogeneous			97.0
0.50	0.489	1.455	1.743	270.9	29.91	0.50	0.434	1.463	1.990	332.2	97.0
0.55	0.506	1.364	1.870	263.4	29.84	0.55	0.457	1.394	2.113	322.9	96.60
0.60	0.517	1.275	2.046	251.7	29.74	0.60	0.469	1.303	2.312	307.3	96.04
0.65	0.533	1.205	2.244	235.3	29.53	0.65	0.483	1.229	2.584	286.8	95.17
0.70	0.552	1.146	2.491	214.8	29.22	0.70	0.504	1.171	2.809	261.4	93.70
0.75	0.579	1.101	2.752	189.3	28.68	0.75	0.528	1.121	3.143	231.3	91.77
0.80	0.616	1.068	3.048	160.4	27.87	0.80	0.559	1.080	3.562	196.2	89.05
0.85	0.666	1.042	3.399	127.3	26.75	0.85	0.602	1.047	4.098	155.9	85.15
0.90	0.730	1.021	3.903	90.2	25.30	0.90	0.667	1.022	4.794	109.8	79.45
0.95	0.820	1.002	4.784	46.7	23.35	0.95	0.758	1.000	6.308	55.9	72.00
1.00					20.1	1.00					57.6

usually the least reliable measurement in phase equilibrium studies, probably no accuracy is lost and time is gained by omitting this measurement, particularly at low pressures. Vapor phase compositions were calculated by the total pressure method (*1*, *2*, *4*), in which the Gibbs-Duhem equation is integrated at constant temperature using pressure-composition data.

Two computer programs were used to carry out the numerical integration. One used the method of Boissonnas (*2*). Starting with $x_2 = 0$, p_2 for the first equally spaced increment of X is obtained by assuming that the other component obeys Raoult's law, so that

$$\Delta p_2 = \Delta P + p_1^\circ \Delta x_2 \tag{1}$$

in which p_2 and x_2 are the partial pressure and mole fraction of component 2. P is the total pressure and p_1° is the vapor pressure of pure component 1. Succeeding increments are obtained from the equation,

$$\Delta P_2 = \frac{\Delta P}{1 - \dfrac{p_1 x_2}{p_2 x_1}} \tag{2}$$

in which p_1, p_2, x_1, and x_2 are the values at the beginning of the increment. This is a rather crude approximation, but in many instances it gives results as good as theoretically better approximations. The second program integrated the Gibbs-Duhem equation in the form

$$\ln \gamma_2 = -\frac{x_1}{x_2} \ln \gamma_1 + \int_0^{x_1} \frac{\ln \gamma_1}{x_2} dx_1 \tag{3}$$

The value of the activity coefficient, γ_1, at infinite dilution was obtained by assuming that the other component obeyed Raoult's law and extrapolating $p_1/(x_1 p_1^\circ)$ to $x_1 = 0$.

By substituting an integration formula such as the trapezoidal rule or Simpson's rule into Equation 3, an expression of the following form may be obtained:

$$\ln \gamma_2 = A + B \ln \gamma_1 \tag{4}$$

in which A and B are constants. This is solved simultaneously with the relation

$$P = x_1 p_1^\circ \gamma_1 + x_2 p_2^\circ \gamma_2 \tag{5}$$

to obtain γ_1 and γ_2 for each value of x. For the first increment the trapezoidal rule was used; after that, Simpson's rule. Both programs assume that the gas phase is ideal.

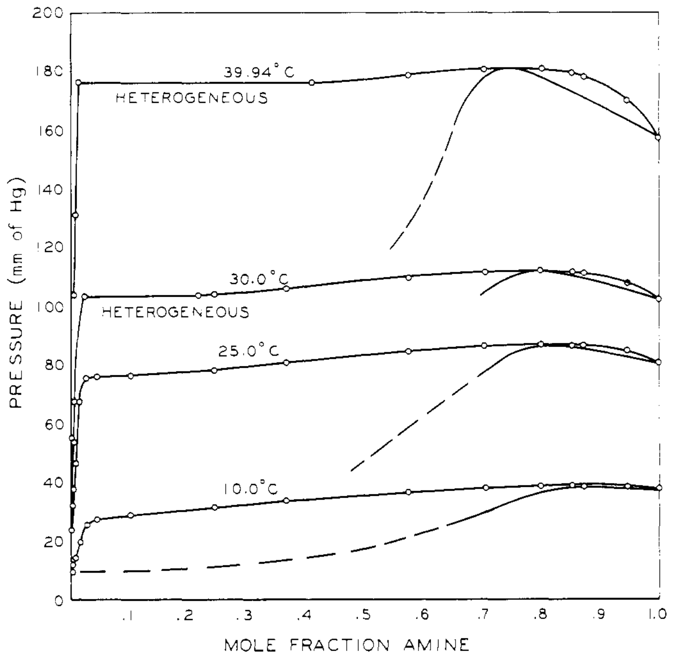

Figure 1. Pressure-composition data for diisopropylamine-water

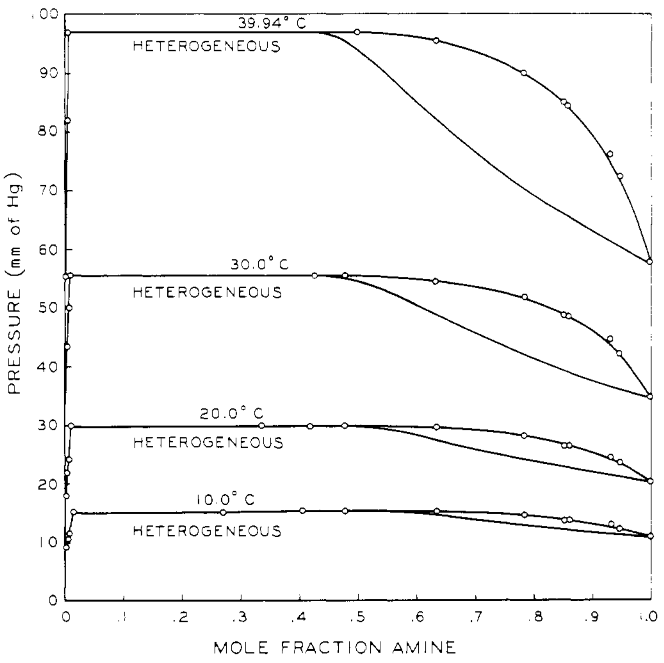

Figure 2. Pressure-composition data for di-*n*-propylamine–water

Both Equations 2 and 3 become indeterminate at an azeotrope. For azeotropic systems the pressure curve must be integrated from each extreme to the azeotrope.

To obtain the pressure for equally spaced values of the mole fraction, the experimental data in Tables II and III were plotted on large scale graph paper and values of P at intervals of 0.025 mole fraction were taken from these graphs. The corresponding values of x and P were used in the numerical integration.

In the second program (Equations 3, 4, and 5) the increment size was altered as a heterogeneous region was approached, so as to terminate exactly at the saturation concentration. The activity coefficient at the other side of the immiscible region was determined by equating γx for the equilibrium liquid phases. The interval was again altered to obtain a succeeding value of x divisible by 0.025. The trapezoidal rule was used in the immediate neighborhood of the heterogenous region.

The results in Tables IV and V were obtained from both programs. In general, for amine concentrations greater than the azeotropic concentration, the data were integrated by the program using Equations 1 and 2. The other side of the curve was integrated with the other program when it was necessary to span a heterogenous region or when a better match at the azeotrope was obtained.

The extreme flatness of these curves causes some problems. It makes it very difficult to pick the correct azeotropic composition, and it makes the calculations very sensitive to errors in the pressure curve. Pressure differences of a few hundredths of a millimeter can make a significant difference in the calculated vapor composition, and the accuracy of the data is only about 0.1 mm. Very minute changes in the total pressure can significantly improve agreement at the azeotrope. The mismatch at the azeotrope is always less than 1 mole %, however, and the two programs agree everywhere within 1 mole %.

The difficulty at the azeotrope could be avoided by using the method of Barker (*1*), except that it requires an analytical expression which can accurately represent the data. A 10-constant Redlich-Kister equation will not fit the amine-water data within the accuracy of the measurements.

Some of the results are shown in Figures 1 and 2. The points are experimental pressure-composition data, except for those on each side of the heterogeneous regions. These show the limits of the miscibility gap. The pressures within the partially miscible region were obtained from data omitted from the graphs. The broken lines are extrapolations. This portion of the vapor composition curve can be calculated from pressure-liquid composition data with good accuracy by assuming that water obeys Raoult's law.

NOMENCLATURE

G^E = excess Gibbs free energy, cal./g. mole
P = total pressure, mm. of Hg
p = partial pressure, mm. of Hg
x = mole fraction in liquid
y = mole fraction in vapor

Greek Letter

γ = activity coefficient

Subscripts

1 = component 1 or amine
2 = component 2 or water

Superscript

° = pure component

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