Vapor-Liquid Equilibria in System Ammonia-Water at 14.69 and 65 Psia

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Isobaric vapor-liquid equilibria of the system NH_3-H_2O were experimentally determined at 14.69 and 65 psia by means of a recirculating still. The concentration ranges investigated were lower than those reported in the literature. The results obtained were correlated in terms of the relative volatility α.

Determination of vapor-liquid equilibria in the ammonia-water system at low concentrations of ammonia in the liquid phase was made to obtain data needed for the design of a certain industrial process. Although equilibrium values of this mixture have been reported in the literature (*2, 3, 5, 7–11, 13*), the conditions reported and the concentration ranges investigated are usually different from those of this study. The work of Clifford and Hunter (*2*) covers this system at temperatures up to 150°C and at pressures up to 20 atm. Although they did report data at 1 atm, no direct comparison can be made, because the smallest liquid composition reported in their work is out of the range of this study. For this reason, the work now reported was carried out to extend the knowledge of this system at lower concentrations at two isobaric conditions.

Experimental

Operation of still. Vapor-liquid equilibrium measurements were made by means of a modified Dvorak and Boublik still. The operating procedure and the description of the still have been reported (*1, 12*). The volume of mixture required to fill the still is about 100 ml. The liquid was boiled continuously for about 3 hr at the desired pressure to ensure that equilibrium was reached.

For measurements at atmospheric pressure, the still was connected to a constant-pressure system which was maintained at 760 ± 0.04 mm Hg. Samples of the equilibrium phases were taken by means of 10-ml syringes. During the sampling procedure, the still was slightly pressurized with air to avoid any possible loss of ammonia.

For measurements at 65 $lb/in.^2$ abs., the glass still was placed in a steel box, which was pressurized with nitrogen to the desired pressure. The pressure of cooling water, measured at the outlet, was carefully maintained at the system pressure to avoid any pressure head on the fragile glass apparatus. The still box was designed and equipped with transparent windows so that the performance of the still could be visually observed. Sampling devices were arranged in such a manner that samples of both the liquid and the vapor phases could be taken without affecting the system pressure and without opening the steel box. Samples of the equilibrium phases were taken through two capillaries. A calibrated Texas Instrument pressure gage (Model 144) was used for pressure measurement. The system pressure was maintained at 65 ± 0.02 $lb/in.^2$ abs.

Temperature measurements were made by means of a calibrated Pt resistance thermometer (Tinsley type no. 5187 H) together with a Guildline resistance compensator (Model 9810 L). The precision of temperature measurements is estimated to be within ±0.01°C.

Materials. Aqueous ammonia solution, approximately 30 wt % of ammonia and supplied by Baker Chemical Co., was used in this study. Distilled water was used to dilute the aqueous ammonia. "Dilut-It" analytical concentrates supplied by Baker Chemical Co. were standardized using "Ultrex" Na_2CO_3 standard supplied by the same company.

Analytical procedure. The sample was introduced into a known volume of 0.1*N* HCl solution (usually 50 ml), and its amount was determined by weighing. Subsequently, it was neutralized by 0.1*N* NaOH solution. A slight excess of 0.1*N* NaOH solution (1–2 ml) was added and then titrated again by 0.1*N* HCl solution to reach the end point, with methyl orange as the indicator. The 0.1*N* HCl was standardized against sodium carbonate, following in detail the procedure presented in the literature (*4*). The 0.1*N* NaOH solution was standardized against the 0.1*N* HCl solution. Precision of the ammonia concentration determinations is believed to be better than ±0.3%.

Results

The experimentally determined values of *T, p, x,* and *y* for the system ammonia-water are listed in Tables I and II for the low and high pressures, respectively. Relative volatility α of the system was correlated by means of the following expression (*6*):

$$\alpha = y_1x_2/y_2x_1 = (1 + a_{12}x_2)/(1 + a_{21}x_1) \qquad (1)$$

Values of the coefficients a_{12} and a_{21} obtained for the concentration range investigated are as follows:

	a_{12}	a_{21}
14.69 psia	12.835 ± 0.061	−7.591 ± 1.810
65. psia	9.146 ± 0.060	−4.523 ± 0.857

These values are recommended only for the purpose of interpolation. Mole fractions of ammonia in the vapor phase are also calculated using the α values obtained by means of the following expression:

$$y_{\text{calc}} = \frac{\alpha x_1/x_2}{1 + \alpha x_1/x_2} \qquad (2)$$

and compared with the experimental values reported in Tables I and II. The standard errors obtained are 0.0023 and 0.0020 for the low and high pressures, respectively.

An attempt was made to compare the experimental data obtained in this study at atmospheric pressure with those reported by Clifford and Hunter (*2*). At this pressure, the lowest temperature studied in this work (90.73°C) is only slightly higher than the highest temperature (90°C) measured by Clifford and Hunter. However, the difference in the ammonia concentration in the vapor phase amounts to 3.7 wt %, indicating the existence of some discrepancy between the two sets of data around 90°C.

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Table I. Vapor-Liquid Equilibria of Ammonia–Water Mixtures at Atmospheric Pressure

NH_3, wt %					
Liquid	Vapor	Temp, °C	x_1	y_1	$y_{calc} - y_1$
0.097	1.280	99.65	0.00103	0.0135	0.0006
0.146	1.937	99.46	0.00150	0.0205	0.0001
0.276	3.739	98.94	0.00292	0.0395	0.0002
0.308	4.129	98.80	0.00326	0.0436	0.0006
0.368	5.188	98.08	0.00389	0.0547	−0.0021
0.482	6.499	98.08	0.00510	0.0685	−0.0001
0.634	8.284	97.51	0.00670	0.0872	0.0019
0.665	9.120	96.90	0.00703	0.0960	−0.0027
1.199	15.80	94.84	0.01267	0.1656	−0.0030
1.445	18.80	93.90	0.01527	0.1967	−0.0037
1.950	24.02	92.00	0.02060	0.2506	0.0022
2.343	28.10	90.73	0.02475	0.2925	0.0045

Standard error = 0.0023

Table II. Vapor-Liquid Equilibria of Ammonia–Water Mixtures at 3361 mm Hg (65 Psia)

NH_3, wt %					
Liquid	Vapor	Temp, °C	x_1	y_1	$y_{calc} - y_1$
0.089	0.844	146.94	0.00094	0.0089	0.0006
0.185	1.831	146.58	0.00196	0.0193	0.0003
0.366	3.821	145.82	0.00387	0.0403	−0.0019
0.693	6.764	144.78	0.00733	0.0713	0.0002
1.061	10.26	143.35	0.01122	0.1079	−0.0007
1.545	14.71	141.52	0.01633	0.1543	−0.0023
1.793	16.95	140.91	0.01895	0.1776	−0.0036
2.188	19.76	139.86	0.02311	0.2067	0.0013
2.258	20.56	139.27	0.02385	0.2149	−0.0011
3.969	33.16	133.91	0.04189	0.3442	0.0008
4.025	33.23	134.73	0.04248	0.3449	0.0040

Standard error = 0.0020

Nomenclature

a_{12}, a_{21} = coefficients, Equation 1
p = system pressure
T = temperature
x = liquid mole fraction
y = vapor mole fraction
α = relative volatility

Subscript

1 = ammonia
2 = water

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