Vapor−Liquid Equilibria for Ammonia + Methanol

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Total pressure measurements for ammonia + methanol were made at 10 °C and 20 °C. The liquid and vapor compositions were derived by iteration from the material balance and the Martin−Hou equation of state.

Introduction

This work constitutes a contribution to Project 805, Experimental Data on Mixtures, of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. The aim of this project is to sponsor solubility, vapor−liquid equilibrium, and infinite dilution activity coefficient measurements on mixtures of industrial importance.

In the production of amine using ammonia and methanol, the unreacted ammonia and methanol must be recovered. Distillation at atmospheric pressure is currently used for the process. However, separation at elevated pressure might be suitable from the viewpoint of energy requirements because the amine process is operated at elevated pressures.

Inomata et al. (1988) published vapor−liquid equilibrium (VLE) data for the binary mixtures derived from ammonia, methanol, and water as well as the ternary mixtures. Mixtures of ammonia + methanol have also been studied by Kudo and Toriumi, (1959), Ma and Xu, (1993), and Xu et al. (1995). Brunner (1988) measured the critical $P(T)$ curve.

In this work, P, x measurements for $NH_3 + CH_3OH$ at 10 °C and 20 °C are reported using the total pressure method. The liquid- and vapor-phase compositions were derived by coupling a material balance with a VLE model and iterating until convergence was attained.
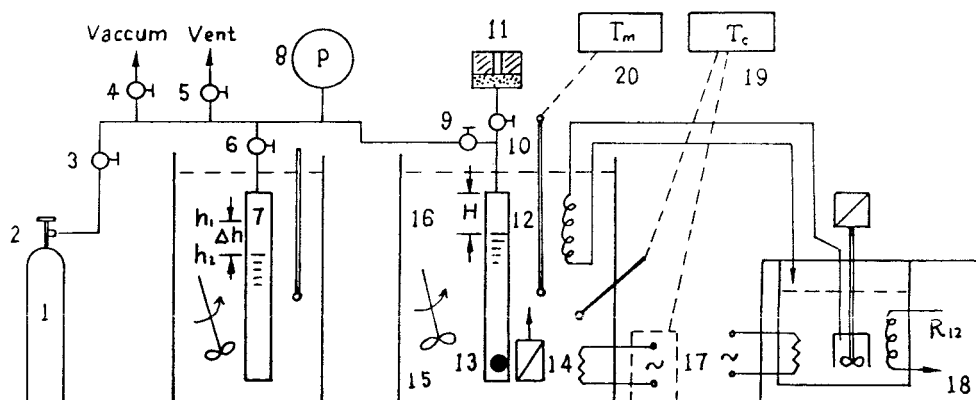
Experimental Section

Materials. Ammonia, purity 99.98%, was from Juzhou Chemical Industry Co.; methanol, purity 99.5% (A. R. grade), was from Shanghi Chemical Agent Factory; and propane, purity 99.99%, was from Dalian Guang Ming Chemical Institute.

Apparatus. A schematic diagram of the apparatus used for the total pressure measurements is shown in Figure 1. It consisted of a feed gas cylinder, a metering tank for the feed, an equilibrium cell immersed in a constant-temperature water bath and a low-temperature bath. The equilibrium cell and the metering tank were made of Pyrex. The two ends of the tube were enclosed with stainless steel flanges and Teflon sealing washers. The contents of the cell were stirred with a small iron ball moved up and down by moving a magnetic iron block outside the cell. The required cooling for the water bath was provided by a low-temperature bath (R12 as refrigerant and industrial ethanol as coolant) and the required heat by an electric heater controlled by a DWT-702 model temperature controller with a Ni−Cr/Ni−Al thermocouple. The temperature of the water bath was measured by a PY-20 model platinum resistance digital thermometer calibrated previously against a standard mercury thermometer. The equilibrium pressures were measured using a Bourdon-tube gauge whose accuracy was checked against a dead weight tester to an accuracy of ±0.01 MPa. The height of the liquid level in the metering tank or in the equilibrium cell was measured by a cathetometer with a precision of ±0.01 mm.

The precision and accuracy of the various measurements and control elements were as follows: temperature control, ±0.05 K; temperature measurement, precision ±0.01 K and accuracy ±0.05 K; pressure measurement, precision ±0.008 MPa and accuracy ±0.01 MPa; height measurement, precision ±0.01 mm and accuracy ±0.1 mm.

Procedure. Valves 3, 4, 6, 9, and 10 were opened, and the system was evacuated with a vacuum pump. The residual air was then removed by purging the system three times with NH_3 at a pressure of about 2 bar, and NH_3 was condensed into the metering tank 7. Valve 9 was closed, and a known mass of methanol, which had been previously degassed by evacuation, was injected into the equilibrium cell 12 through the injection port 11, and valve 10 was closed. Valves 3 and 4 were closed, and the vapor pressure of the ammonia at the metering tank temperature, t_1, was noted on the manometer. The height of the liquid level in the metering tank 7, h_1, was noted using the cathetometer; then valve 9 was opened, and ammonia was slowly transferred into the equilibrium cell until the required pressure was reached. Valve 6 was then closed, the magnetic iron block 14 was moved up and down, and the contents of the cell were stirred by moving the small iron ball until the equilibrium temperature and pressure showed no change. The magnetic stirrer was stopped, and the equilibrium cell temperature, t_2, the pressure, p, and the height, H, of the vapor space at the top of the cell were noted. Valve 9 was then closed and valve 6 opened, letting ammonia into the lines of the system. When the ammonia in the metering tank had equilibrated with the external lines, the height

Figure 1. Schematic diagram of experimental apparatus: (1) cylinder; (2–5, 6, 9, 10) valves; (7) metering tank; (8) manometer; (11) head for injection; (12) equilibrium cell; (13) small iron ball; (14) magnetic iron block; (15) constant-temperature water bath; (16) stirrer with a motor; (17) electric heater; (18) low-temperature bath; (19) temperature controller; (20) thermometer.

h_2 of NH_3 in the metering tank was measured to give Δh. A new measurement was made by repeating the procedure until the equilibrium pressure approached the vapor pressure of pure ammonia.

Data Reduction. For VLE measurements of mixtures containing a highly volatile compound, the accurate measurement of the vapor-phase composition can be difficult. In the total pressure method one can calculate y from T, P, x measurements using a direct method (Van Ness, 1964) and by an indirect method (Mixon et al., 1965).

In this work, the temperature, pressure, and amounts of material concerned with material balance were first measured; then the initial value of the liquid-phase composition was estimated from the knowledge of the material balance. Finally, the liquid and vapor mole fractions were determined by iteration using an equation of state model as follows.

The material balance and the determination of the liquid mole fraction for NH_3 (1) + CH_3OH(2) are given by

ammonia balance: $\quad m_1^T = m_1^v + m_1^l$

methanol balance: $\quad m_2^T = m_2^v + m_2^l$

where m_i^v and m_i^l are the masses of component i in the vapor and liquid phases

$$m_1^T = \frac{\pi}{4} d_1^2 \Delta h \{\rho^l(t_1) - \rho^v(t_1)\} \approx \Delta V \rho^l(t_1) \qquad (1)$$

$$m_1^v = \frac{\pi}{4} d_2^2 H \rho_m^v(t_2)\, w_1 = V \rho^v(t_2)\, w_1 \qquad (2)$$

$$m_2^T = m_2 \qquad (3)$$

$$m_2^V = m_1^V (1 - w_1)/w_1 \qquad (4)$$

where d_1 and d_2 are the diameters of the glass tubes in the metering tank and equilibrium cell, respectively, $\rho^l(t_1)$ is the density of liquid ammonia at temperature t_1, $\rho_m^v(t_2)$ is the density of the vapor mixture at t_2, Δh is the height change of liquid ammonia in the metering tank, and H is the height of the vapor space above the liquid in the equilibrium cell; w_i is the mass fraction of component i.

$$w_1 = y_1 M_1 / \{y_1 M_1 + (1 - y_1) M_2\} \qquad (5)$$

$$x_1 = (m_1^l/M_1)/(m_1^l/M_1 + m_2^l/M_2) \qquad (6)$$

where x_1 and y_1 are the mole fractions of component 1 in the liquid and vapor phases, respectively. M_i is the molecular weight of component i, so that

$$x_1 = f(y_1) \qquad (7)$$

When $y_1 = 1$, $x_1 = 1$, and $\rho_m^v(t_2) = \rho_1^v(t_2)$. For equilibrium in the vapor and liquid phases

$$\hat{\varphi}_i^v p y_i = \hat{\varphi}_i^l p x_i \qquad (8)$$

with the additional constraints

$$\sum_i y_i = \sum_i x_i = 1 \qquad (9)$$

where $\hat{\rho}_i^v$ and $\hat{\rho}_i^l$ are the fugacity coefficients in the gas and liquid phases, were calculated using the Martin−Hou equation of state (Martin and Hou, 1955).

$$p = RT/(v - b) + \sum_{k=2}^{5} f_k(T)/(v - b)^k \qquad (10)$$

where

$$f_k(T) = A_k + B_k T + C_k \exp\left[-5.475\frac{T}{T_c}\right] \qquad (11)$$

$$C_4 = A_5 = C_5 = 0$$

The constants A_k, B_k, and, C_k for the pure components were calculated from critical properties and vapor pressure data (Hou et al., 1981, 1982, Lu, 1982).

For mixtures, the following mixing rules apply.

$$f_2(T) = -\sum_i \sum_j x_i x_j f_2(T)_{ij} \qquad (12)$$

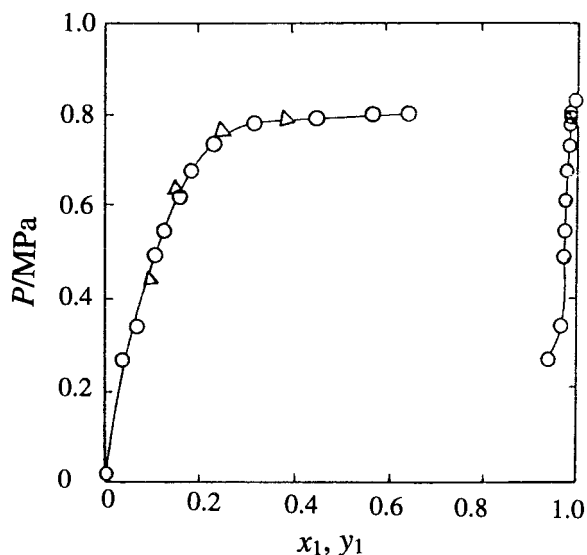$$f_2(T)_{ij} = [f_2(T)_i\, f_2(T)_j]^{1/2}(1 - k_{ij}) \qquad (13)$$

$$f_k(T) = (-1)^{k-1}\{\sum_i x_i f_k(T)_i^{1/k}\}^k \qquad (14)$$

The fugacity coefficient is given by

$$\ln \hat{\varphi}_i^l = Pb_i^l/RT = \ln\{P(v^1 - b_1)/RT\} + \frac{1}{RT}\sum_{k=2}^{5} \frac{E_k(T)_i}{(v^1 - b^1)^{k-1}} \qquad (15)$$

Table 1. Vapor−Liquid Equilibria for NH₃ (1) + CH₃OH (2)

		vapor		calc			
P/MPa	Vl(NH₃)/cm³	V/cm³	$\rho^v(t_2)$/(g·cm⁻³)	x_1	y_1	P/MPa	$100\Delta\rho/\rho$
		$t_2 = 10\ °C$; t_1(NH₃) = 20.7 °C; $\rho^l(t_1)$ = 0.6091 g·cm⁻¹; m_2 = 3.3367 g; k_{ij} = 0.014 04					
0.13	1.5986	12.4633	1.2677	0.351	0.960	0.125	3.8
0.18	2.3354	11.7884	1.6489	0.442	0.972	0.17	2.8
0.23	2.9598	11.1134	2.0242	0.501	0.978	0.22	4.3
0.28	3.9589	10.6226	2.2790	0.574	0.984	0.27	3.6
0.30	4.6583	9.7635	2.4107	0.614	0.986	0.30	0
0.33	5.4951	8.9045	2.5345	0.652	0.988	0.33	0
0.36	6.4317	8.0455	2.6799	0.687	0.990	0.37	−2.8
0.38	7.1561	7.4932	2.8691	0.710	0.991	0.39	−2.6
0.41	8.4549	6.3274	3.1202	0.743	0.992	0.42	−1.2
		$t_2 = 20\ °C$; t_1(NH₃) = 19.5 °C; $\rho^l(t_1)$ = 0.6109 g·cm⁻³; m_2 = 3.3890 g; k_{ij} = 0.002 73					
0.10	1.0615	12.3406	0.7494	0.236	0.865	0.096	4.0
0.19	1.9982	10.8680	1.7119	0.368	0.974	0.18	5.3
0.25	2.8100	10.317	2.2613	0.450	0.962	0.25	0
0.32	3.5593	9.3954	2.2983	0.510	0.970	0.32	0
0.39	4.3711	8.5363	3.0828	0.561	0.975	0.385	1.3
0.45	5.1454	7.9841	3.4508	0.601	0.979	0.44	2.2
0.50	6.6440	7.1864	3.7084	0.661	0.982	0.505	−1.0
0.53	7.5182	6.0820	3.9433	0.689	0.985	0.54	−1.9
0.56	8.3925	5.4070	4.1742	0.712	0.987	0.56	0

Figure 2. Comparison between this work and literature data for propane (1) + methanol (2): △, this work; ○, Nagahama et al. (1971).

where

$$E_2(T)_i = 2\sum_j x_j f_2(T_1)_{ij} \tag{16}$$

$$E_k(T)_i = \frac{Kf_K(T)}{K-1} \cdot \left\{ \frac{f_K(T)_i}{f_K(T)} \right\}^{1/k} \tag{17}$$

The binary interaction parameters k_{ij} were determined from the material balance and phase equilibrium condition by iteration, using the objective function OF.

$$OF = \min\left\{ \sum_{i=1}^N \left(1 - \frac{P_{calc}}{P_{expt}} \right)^2_i \right\} \tag{18}$$

To test the apparatus and technique, measurements were made on the well-characterized system propane + methanol at 19.9 °C. The results given in Figure 2 show good agreement with literature values (Nagahama et al., 1971).
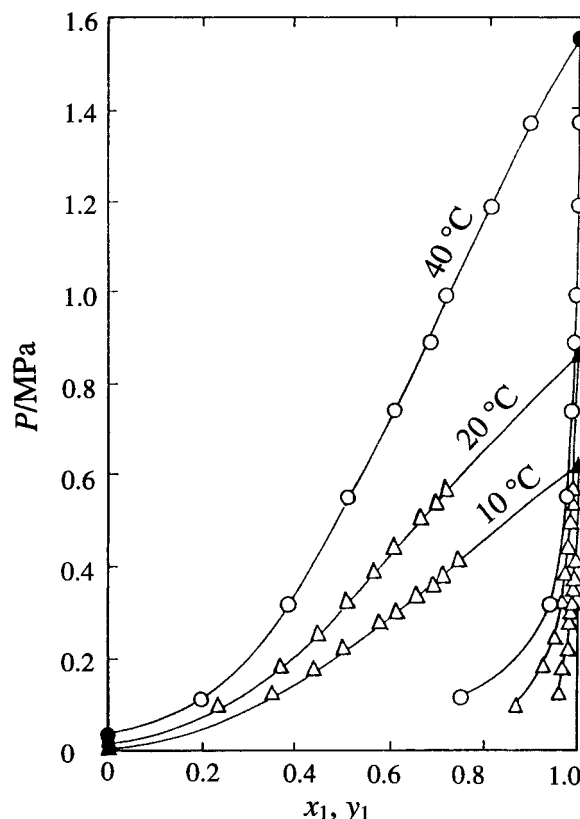
Figure 3. Comparison between this work and literature data for ammonia (1) + methanol (2): △, this work; ○, Inomata et al. (1988).

Results

The liquid and vapor compositions for ammonia + methanol at 10 °C and 20 °C given in Table 1 were calculated from the data reduction method described above. The results are compared with literature data (Inomata et al., 1988) in Figure 3.

Conclusion

An apparatus for measuring vapor−liquid equilibria by the total pressure method was used to measure the test system propane + methanol at 19.9 °C. The results are in good agreement with literature values.

The total pressure method was used for the ammonia + methanol system at 10 °C and 20 °C. The (P, T, x, y) data were derived by coupling material balance with a VLE model and iterating until convergence was attained.

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