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Vapor Pressures and Liquid Densities of Ammonium Chloride + Ammonia Mixtures

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Vapor pressures and liquid densities for ammonium chloride (NH_4Cl) + ammonia (NH_3) mixtures were measured over a wide range of temperatures and concentrations. Vapor pressures of the $NH_4Cl + NH_3$ mixtures were measured at temperatures ranging from (303.12 to 373.16) K and concentrations ranging up to 50.74 wt % of NH_4Cl. Vapor pressure was measured with a pressure transducer. The experimental values were correlated with Antoine's equation. Liquid densities of the $NH_4Cl + NH_3$ mixtures were measured at temperatures ranging from (303.15 to 373.15) K, pressure ranging from (10.0 to 30.0) MPa, and concentrations ranging up to 50.68 wt % of NH_4Cl. Liquid densities were measured with a piezometer. The experimental values were correlated with a Tait-form equation.

Introduction

Recently, gallium nitride (GaN) has attracted considerable attention for various optoelectronic devices as suitable material. Therefore, high quality GaN crystal is required. There are only few methods for preparing GaN bulk crystals such as N_2 high-pressure method, Na-flux method, and the ammonothermal method.[1] The ammonothermal method is one of the most promising methods for crystal growth of GaN. In this process, NH_3 and NH_4Cl are used as solvent and mineralizer, respectively.[2] However, there are a few data regarding the thermophysical properties of $NH_4Cl + NH_3$ mixture. Several researchers reported the vapor pressures of $NH_4Cl + NH_3$ mixture at low temperature range.[3–5] The vapor pressures over a wide temperature range and at various concentrations have not been reported yet.

In this paper, vapor pressures and liquid densities for $NH_4Cl + NH_3$ were measured. Vapor pressures of $NH_4Cl + NH_3$ mixture were measured at temperatures ranging from (303.12 to 373.16) K and concentrations ranging up to 50.74 wt % of NH_4Cl. Liquid densities of $NH_4Cl + NH_3$ mixture were measured at temperatures ranging from (303.15 to 373.15) K, pressure ranging from (10.0 to 30.0) MPa, and concentrations ranging up to 50.68 wt % of NH_4Cl.

Experimental Section

Materials. NH_4Cl which had minimum purities 99 % was purchased from Wako Pure Chemical Industries. It was dried at 373.15 K for 6 h before measurement.

The ammonia gas of 99.999 % purity was supplied by Japan Fine Products Co. Ltd. The samples were used without further purification.

Vapor Pressure Measurements. Experimental Apparatus. The schematic diagram of the experimental apparatus is shown in Figure 1.

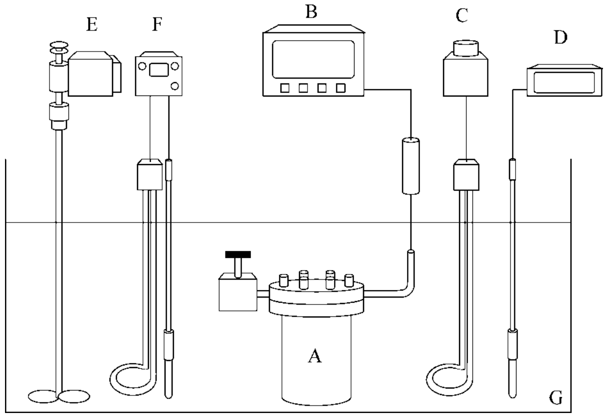

Figure 1. Schematic outline of the experimental apparatus: A, stainless-steel pressure-resistant cell; B, digital pressure gauge; C, heater; D, quartz thermometer; E, motor; F, temperature controller; G, thermostatic bath.

Table 1. Experimental Results of the Vapor Pressures of Ammonia

T/K	P/MPa	P_{calc}/MPa [12]
303.12	1.166	1.167
313.14	1.553	1.555
323.16	2.030	2.035
333.13	2.609	2.613
343.13	3.305	3.310
353.13	4.132	4.137
363.12	5.105	5.110
373.16	6.243	6.254

The volume of the stainless-steel pressure-resistant cell was determined with the gas expansion method[6] using N_2 gas and was 65.22 ± 0.02 cm^3 at 298.15 K. The temperature of the oil bath was regulated within ± 20 mK by using a temperature controller and was measured with a quartz thermometer (Tokyo Denpa, Co., DMT-610). The temperature of the sample would be equal to the temperature of the oil bath. The vapor pressures were measured with a pressure transducer (Paroscientific, Inc., 46k-101) with an accuracy of ± 0.001 MPa, which was calibrated against a dead weight gauge. The uncertainty of concentration of NH_4Cl was 0.05 wt %. The uncertainty of the reported vapor pressure values is estimated to be ± 0.5 %.

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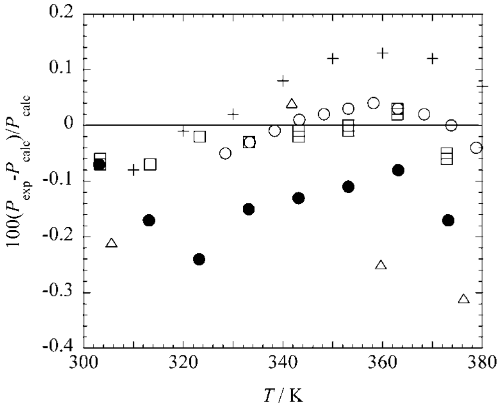

Figure 2. Deviations of the experimental vapor pressure data from the calculated values from the extended corresponding-states principle proposed by Xiang.[12] ○, ref 8; □, ref 9; △, ref 10; +, ref 11; ●, this work.

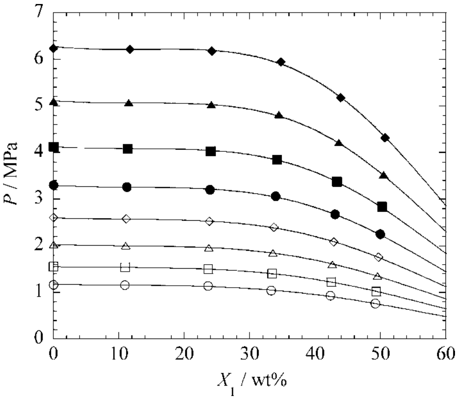

Figure 3. Comparison of the vapor pressure data for the ammonium chloride + ammonia mixture with results from the Antoine's equation. ○, 303.12 K; □, 313.14 K; △, 323.16 K; ◇, 333.13 K; ●, 343.13 K; ■, 353.13 K; ▲, 363.12 K; ◆, 373.16 K; —, correlations.

Table 2. Experimental Results of the Vapor Pressures of Ammonium Chloride + Ammonia Mixture

T/K	X_1/wt %	P/MPa	T/K	X_1/wt %	P/MPa
303.12	10.91	1.155	303.12	23.63	1.140
313.14	10.98	1.538	313.14	23.69	1.500
323.16	11.05	2.002	323.16	23.76	1.959
333.13	11.14	2.573	333.13	23.84	2.524
343.13	11.24	3.261	343.13	23.92	3.203
353.13	11.36	4.088	353.13	24.01	4.032
363.12	11.50	5.065	363.12	24.13	5.022
373.16	11.66	6.212	373.16	24.24	6.176
303.12	33.28	1.043	303.12	42.32	0.932
313.14	33.41	1.400	313.14	42.46	1.222
323.16	33.56	1.843	323.16	42.62	1.598
333.13	33.74	2.399	333.13	42.82	2.084
343.13	33.94	3.063	343.13	43.05	2.674
353.13	34.16	3.858	353.13	43.30	3.380
363.12	34.45	4.815	363.12	43.61	4.208
373.16	34.75	5.941	373.16	43.93	5.177
303.12	49.23	0.764			
313.14	49.36	1.017			
323.16	49.54	1.350			
333.13	49.73	1.756			
343.13	49.95	2.250			
353.13	50.20	2.839			
363.12	50.46	3.525			
373.16	50.74	4.317			

Table 3. Antoine's Equation Parameters

a_0	4.3775	b_0	1482.65
a_1	-3.4951×10^{-3}	b_1	-0.99660
a_2	2.8276×10^{-4}	b_2	8.7545×10^{-2}
a_3	-2.4356×10^{-7}	b_3	2.4240×10^{-4}
a_4	-6.7296×10^{-8}	b_4	-1.6565×10^{-5}

Experimental Method. The stainless-steel pressure resistant cell was dried at 373.15 K under vacuum for 2 h to remove moisture. Then, a weighed amount of the NH_4Cl and a stirring bar are charged in the cell. The valve and transducer were attached with the cell. After degassing for about 5 min, the NH_3 was introduced into the cell with a plunger pump. The amount of NH_3 charged in the cell was determined by weighing the cell with the electrical balance, accurate to within 0.01 g, before and after loading NH_3. After introducing NH_3 and weighing the cell, the $NH_4Cl + NH_3$ mixture was stirred with a magnetic stirring bar for 1 h to dissolve NH_4Cl in NH_3. Then, the cell was immersed in the oil bath.

In this study, we used a static method for vapor pressure measurement. Therefore, the concentration was changed at each temperature. The concentration of liquid mixture was determined as follows. The two assumptions were adopted: (1) NH_4Cl does not exist in the vapor phase; (2) the vapor phase is ideal. The amounts of NH_4Cl and NH_3 and the volume of the cell were known experimentally. Therefore, if the density of liquid mixture was known, we can evaluate the volumes of vapor and liquid phase. Therefore the concentration of the NH_4Cl in the NH_3 solution is determined by a material balance. It should be mentioned that the vapor phase should be as small as possible to reduce the effect of ambiguity of assumption (2).

Because the pressure sensor cannot be immersed into the bath liquid, we connected the sensor to the cell with a high pressure tubing of 0.016 cm inner diameter. We also tried to make the length of the tubing from the oil bath to the pressure sensor as short as possible (about 5 cm). As a result, the inner volume of the tubing and the pressure sensor above the bath liquid being functioned as a dead volume is estimated to be 0.001 cm^3, which is less than about 0.002 % to the vapor phase volume in the cell. Furthermore, we did not observe NH_3 condensation phenomena in the part of the tubing and the pressure sensor. So we considered that the effect of the dead volume on the concentration determination is negligible.

Liquid Density Measurements. Experimental Apparatus. The liquid densities of $NH_4Cl + NH_3$ mixture were measured with a glass piezometer, which has been described in detail elsewhere.[7]

Experimental Method. Weighed NH_4Cl was charged in the glass cell, and the valve was attached with the glass cell. After degassing for about 5 min, NH_3 was introduced into the glass cell from the valve by immersing the glass cell in the methanol, which was cooled at about 233 K. The amount of NH_3 charged in the cell was determined by weighing the cell with the electrical balance, accurate to within 0.001 g, before and after loading NH_3. After dissolving NH_4Cl in NH_3, the glass cell was set into the pressure vessel.

The sample cell volume was approximately 13 cm^3. The estimated uncertainties in the liquid densities are ± 0.2 %.

Results and Discussion

Vapor Pressure Measurement of $NH_4Cl + NH_3$ Mixture. To clarify the reliability of our measurement apparatus, the vapor pressures of ammonia were measured. The experimental results of the vapor pressures of ammonia are given in Table 1. Figure 2 shows the deviations of the experimental vapor pressure data in the literature[8–11] from the values calculated by the extended corresponding-states principle proposed by Xiang.[12] The extended corresponding-states principle represents our results

Table 4. Experimental Results of the Liquid Densities of Ammonium Chloride + Ammonia Mixture.

T	X_1	P	ρ	T	X_1	P	ρ	T	X_1	P	ρ	T	X_1	P	ρ
K	wt %	MPa	$kg \cdot m^{-3}$	K	wt %	MPa	$kg \cdot m^{-3}$	K	wt %	MPa	$kg \cdot m^{-3}$	K	wt %	MPa	$kg \cdot m^{-3}$
303.15	11.33	10.0	668.2	313.15	11.33	10.0	655.5	343.15	11.33	10.0	613.4	353.15	11.33	10.0	597.6
		15.0	673.3			15.0	660.5			15.0	620.3			15.0	605.7
		20.0	677.8			20.0	665.3			20.0	627.1			20.0	612.9
		25.0	682.2			25.0	670.1			25.0	633.1			25.0	619.7
		30.0	686.7			30.0	674.6			30.0	638.6			30.0	626.1
	22.24	10.0	729.3		22.24	10.0	716.0		22.24	10.0	682.5		22.24	10.0	669.2
		15.0	733.1			15.0	720.5			15.0	688.1			15.0	675.5
		20.0	736.6			20.0	725.1			20.0	692.5			20.0	680.2
		25.0	740.1			25.0	729.5			25.0	696.9			25.0	684.7
		30.0	743.8			30.0	734.2			30.0	701.2			30.0	689.2
	31.34	10.0	787.8		31.34	10.0	778.1		31.34	10.0	745.7		31.34	10.0	735.4
		15.0	791.5			15.0	783.6			15.0	751.6			15.0	741.5
		20.0	795.8			20.0	786.8			20.0	755.0			20.0	746.5
		25.0	798.5			25.0	789.7			25.0	758.3			25.0	750.3
		30.0	801.6			30.0	792.5			30.0	761.1			30.0	754.0
	42.85	10.0	833.0		42.85	10.0	825.9		42.85	10.0	801.9		42.85	10.0	793.4
		15.0	836.1			15.0	828.4			15.0	805.2			15.0	796.6
		20.0	838.2			20.0	831.0			20.0	807.6			20.0	799.5
		25.0	840.8			25.0	833.5			25.0	810.0			25.0	801.9
		30.0	842.9			30.0	835.6			30.0	812.0			30.0	804.2
	50.68	10.0	873.3		50.68	10.0	867.9		50.68	10.0	846.0		50.68	10.0	838.0
		15.0	877.7			15.0	871.7			15.0	850.6			15.0	844.0
		20.0	880.4			20.0	874.4			20.0	854.2			20.0	847.5
		25.0	883.2			25.0	876.6			25.0	857.4			25.0	850.1
		30.0	885.4			30.0	878.8			30.0	859.7			30.0	852.7
323.15	11.33	10.0	642.7	333.15	11.33	10.0	628.8	363.15	11.33	10.0	581.2	373.15	11.33	10.0	568.8
		15.0	648.4			15.0	634.7			15.0	588.8			15.0	577.2
		20.0	654.2			20.0	640.8			20.0	596.4			20.0	585.5
		25.0	658.7			25.0	646.7			25.0	603.4			25.0	593.0
		30.0	663.4			30.0	652.3			30.0	610.6			30.0	600.3
	22.24	10.0	707.1		22.24	10.0	694.9		22.24	10.0	654.5		22.24	10.0	644.4
		15.0	711.9			15.0	699.8			15.0	661.6			15.0	651.7
		20.0	715.8			20.0	704.3			20.0	667.3			20.0	657.3
		25.0	719.7			25.0	708.7			25.0	672.2			25.0	662.3
		30.0	723.4			30.0	712.9			30.0	677.3			30.0	667.2
	31.34	10.0	767.7		31.34	10.0	756.3		31.34	10.0	724.1		31.34	10.0	713.8
		15.0	772.6			15.0	761.1			15.0	731.7			15.0	721.3
		20.0	776.3			20.0	765.1			20.0	736.8			20.0	726.2
		25.0	779.4			25.0	768.2			25.0	741.5			25.0	730.7
		30.0	782.4			30.0	770.8			30.0	745.7			30.0	734.6
	42.85	10.0	817.4		42.85	10.0	809.5		42.85	10.0	784.2		42.85	10.0	776.9
		15.0	820.9			15.0	812.4			15.0	789.2			15.0	781.3
		20.0	823.4			20.0	814.4			20.0	792.0			20.0	784.1
		25.0	825.9			25.0	817.9			25.0	794.3			25.0	786.5
		30.0	827.4			30.0	820.4			30.0	796.4			30.0	788.7
	50.68	10.0	860.0		50.68	10.0	853.2		50.68	10.0	830.5		50.68	10.0	823.8
		15.0	864.7			15.0	857.9			15.0	837.0			15.0	830.3
		20.0	867.9			20.0	860.5			20.0	840.5			20.0	834.0
		25.0	870.6			25.0	863.1			25.0	843.5			25.0	837.0
		30.0	872.8			30.0	865.3			30.0	846.0			30.0	839.6

within uncertainty. The present experimental values agree with the results of Baehr et al.[8]

The experimental results of the vapor pressures of NH_4Cl + NH_3 mixture are shown in Table 2. There are no literature values in this measurement range.

The vapor pressures were correlated with the Antoine's equation. Yamamoto et al. correlated the vapor pressures of ammonium bromide + ammonia and ammonium iodide + ammonia with Antoine's equation that the Antoine constants for each mixture were expressed as the fourth-degree function of ammonium halide concentration.[13]

$$\log(P/\mathrm{MPa}) = A - \frac{B}{C + T/\mathrm{K} - 273.15} \tag{1}$$

$$A = a_0 + a_1X_1 + a_2X_1^2 + a_3X_1^3 + a_4X_1^4 \tag{2}$$

$$B = b_0 + b_1X_1 + b_2X_1^2 + b_3X_1^3 + b_4X_1^4 \tag{3}$$

$$C = 314.16 \tag{4}$$

where X_1 is concentration of ammonium chloride. The values of these parameters were determined by using the present

Table 5. Tait-Form Equation Parameters

T	X_1		D	T	X_1		D
K	wt %	E	MPa	K	wt %	E	MPa
303.15	11.33	0.1107	62.89	343.15	11.33	0.1026	32.50
	22.24	0.0992	78.78		22.24	0.0627	27.99
	31.34	0.0381	25.02		31.34	0.0300	10.01
	42.85	0.0274	27.47		42.85	0.0188	11.45
	50.68	0.0145	2.89		50.68	0.0189	4.96
313.15	11.33	0.1620	94.61	353.15	11.33	0.1109	29.48
	22.24	0.8893	698.81		22.24	0.0509	16.29
	31.34	0.0161	0.19		31.34	0.0302	5.91
	42.85	0.0585	80.48		42.85	0.0260	19.65
	50.68	0.0138	3.97		50.68	0.0121	−3.54
323.15	11.33	0.0752	28.96	363.15	11.33	0.2314	76.57
	22.24	0.0575	31.84		22.24	0.0552	14.02
	31.34	0.0239	6.88		31.34	0.0316	3.45
	42.85	0.0133	3.28		42.85	0.0109	−3.36
	50.68	0.0137	0.44		50.68	0.0124	−4.02
333.15	11.33	0.2652	127.10	373.15	11.33	0.1655	43.58
	22.24	0.1010	60.49		22.24	0.0506	10.92
	31.34	0.0220	4.69		31.34	0.0285	1.88
	42.85	0.0472	51.43		42.85	0.0138	0.35
	50.68	0.0122	−0.52		50.68	0.0131	−3.67

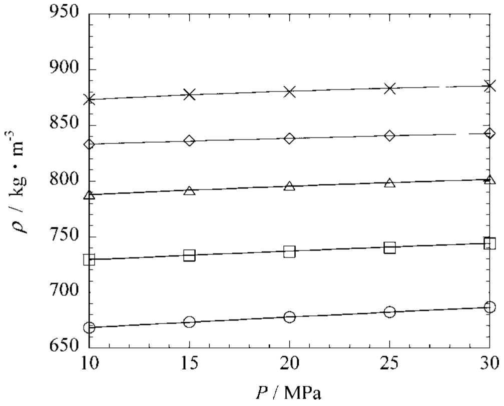

Figure 4. Comparison of the liquid density data for the ammonium chloride + ammonia mixture with results from the Tait-form equation at 303.15 K. ○, 11.33 wt %; □, 22.24 wt %; △, 31.34 wt %; ◇, 42.85 wt %; ×, 50.68 wt %; —, correlations.

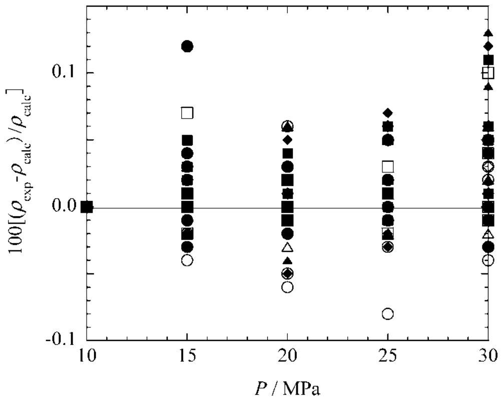

Figure 5. Deviations of the liquid density data from the Tait-form equation. ○, 303.15 K; □, 313.15 K; △, 323.15 K; ◇, 333.15 K; ●, 343.15 K; ■, 353.15 K; ▲, 363.15 K; ◆, 373.15 K; —, correlations.

experimental results with a least-squares method and are listed in Table 3. Comparisons of the vapor pressure data for the $NH_4Cl + NH_3$ mixture with results from the Antoine's equation are shown in Figure 3. The Antoine's equation correlated the experimental values of $NH_4Cl + NH_3$ mixture within ± 1.9 %.

Liquid Density Measurement of $NH_4Cl + NH_3$ Mixture. The experimental results of the liquid densities of $NH_4Cl + NH_3$ mixture are shown in Table 4. The experimental density values were correlated with Tait-form equation.[14]

$$\frac{\rho - \rho_0}{\rho} = E \ln\left(\frac{D + P}{D + P_0}\right) \tag{5}$$

where ρ and ρ_0 are the densities at P and P_0 (= 10.0 MPa), respectively. E and D are adjustable parameters. Table 5 shows the values of the parameters determined by using the present experimental results. Comparisons of the vapor pressure data for the $NH_4Cl + NH_3$ mixture with results from the Tait-form equation at 303.15 K are shown in Figure 4. Figure 5 shows deviations of the experimental data from the Tait-form equation. The Tait-form equation correlated the experimental values of $NH_4Cl + NH_3$ mixture within 0.2 %.

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