Vapor Pressures and Liquid Densities of Ammonium Iodide + Ammonia Mixtures

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Vapor pressures and liquid densities for ammonium iodide (NH_4I) + ammonia (NH_3) mixtures were measured over a wide range of temperatures and molalities. Vapor pressures of the $NH_4I + NH_3$ mixtures were measured at temperatures ranging from (303.12 to 373.16) K and molalities ranging up to 19.314 $mol \cdot kg^{-1}$ of NH_4I. Vapor pressures were measured with a static method. The experimental values were correlated with Antoine's equation. Liquid densities of the $NH_4I + NH_3$ mixtures were measured at temperatures ranging from (303.15 to 373.15) K, pressure ranging from (10.0 to 30.0) MPa, and molalities ranging up to 16.465 $mol \cdot kg^{-1}$ of NH_4I. Liquid densities were measured with a piezometer. The experimental values were correlated with a Tait form equation.

Introduction

Gallium nitride (GaN) has attracted considerable attention as a material for optoelectronic devices such as blue, green, and white light-emitting diodes and high-frequency, high-power transistors. To realize these devices, high-quality and large diameter bulk GaN is required. Several methods have been proposed and tested for the GaN crystal growth.[1–3] The ammonothermal method, which is a solvothermal method, is one of the most promising techniques for achieving this purpose.[2,4–6] In the acidic ammonothermal method, ammonia and ammonium halide are used as a solvent and mineralizer, respectively.[6,7] However, there are few data regarding the thermophysical properties of ammonium halide + ammonia mixtures. The vapor pressures of ammonium bromide + ammonia and ammonium iodide + ammonia solutions over a wide temperature range and at various concentrations were reported by Yamamoto et al.[8] They also reported the liquid densities of these solutions at saturated vapor pressure.[9] However, there are no literature values for liquid densities of these solutions above saturated vapor pressure.

In our previous studies, we measured the vapor pressures and liquid densities of ammonium chloride + ammonia and ammonium bromide + ammonia mixtures.[10,11] The present paper describes continuing work on the experimental determination of the vapor pressures and liquid densities consisting of ammonium halide + ammonia mixtures. In this paper, vapor pressures and liquid densities for ammonium iodide (NH_4I) + ammonia (NH_3) were measured. Vapor pressures of $NH_4I + NH_3$ mixture were measured at temperatures ranging from (303.12 to 373.16) K and molalities ranging up to 19.314 $mol \cdot kg^{-1}$ of NH_4I. Liquid densities of $NH_4I + NH_3$ mixture were measured at temperatures ranging from (303.15 to 373.15) K, pressure ranging from (10.0 to 30.0) MPa, and molalities ranging up to 16.465 $mol \cdot kg^{-1}$ of NH_4I.

Experimental Section

Materials. NH_4I, which had minimum purities of 99.5 mass %, was purchased from Wako Pure Chemical Industries. It was dried at 373.15 K for 12 h before measurement. The NH_3 of 99.999 mol % purity was supplied by Japan Fine Products Co. Ltd. The samples were used without further purification.

Apparatus and Procedure. The vapor pressure was measured with a static method. The experimental apparatus and procedures were the same as those described in our previous study.[10] Temperature and pressure values have an uncertainty of ± 0.02 K and ± 0.001 MPa, respectively. The composition of the sample mixtures were determined by weighting. The uncertainty of the composition determination was estimated to be less than 0.05 mass %. On the basis of the uncertainties of these properties, the uncertainty of the vapor pressure data is estimated to be within ± 0.5 %. The stainless steel pressure-resistant cell was dried at 373.15 K under vacuum for 2 h to remove moisture. Then, weighed amounts of the NH_4I and 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 $NH_4I + NH_3$ mixture was stirred with a magnetic stirring bar for 1 h to dissolve NH_4I in NH_3. Then, the cell was immersed in the oil bath. After it maintained a constant temperature for more than 1 h to achieve equilibrium, the vapor pressure was measured.

In this study, we used a static method for vapor pressure measurement. Therefore, the concentration was changed at each temperature. To obtain the concentration of liquid mixture, two assumptions were adopted: (1) NH_4I does not exist in the vapor phase, and (2) the vapor phase is ideal. The amounts of NH_4I and NH_3 and the volume of the cell were measured 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_4I in the NH_3 solution is determined by a material balance. It should be mentioned that

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Table 1. Experimental Results of the Vapor Pressures for the NH_4I + NH_3 Mixtures

T/K	m/mol·kg^{-1}	P/MPa	T/K	m/mol·kg^{-1}	P/MPa
303.12	0.812	1.154	303.12	1.769	1.142
313.14	0.815	1.535	313.14	1.776	1.506
323.16	0.819	2.000	323.16	1.785	1.965
333.13	0.824	2.569	333.13	1.794	2.525
343.13	0.830	3.256	343.13	1.805	3.201
353.13	0.839	4.068	353.13	1.817	4.003
363.12	0.849	5.029	363.12	1.837	4.950
373.16	0.862	6.177	373.16	1.862	6.066
303.12	3.171	1.096	303.12	4.846	1.034
313.14	3.186	1.448	313.14	4.864	1.346
323.16	3.204	1.891	323.16	4.884	1.757
333.13	3.224	2.431	333.13	4.913	2.260
343.13	3.250	3.081	343.13	4.949	2.864
353.13	3.278	3.855	353.13	4.996	3.577
363.12	3.313	4.765	363.12	5.029	4.410
373.16	3.355	5.893	373.16	5.068	5.364
303.12	7.373	0.866	303.12	10.345	0.640
313.14	7.415	1.131	313.14	10.388	0.861
323.16	7.459	1.473	323.16	10.445	1.135
333.13	7.510	1.896	333.13	10.488	1.456
343.13	7.571	2.403	343.13	10.550	1.840
353.13	7.635	2.982	353.13	10.603	2.303
363.12	7.709	3.654	363.12	10.643	2.825
373.16	7.730	4.411	373.16	10.701	3.431
303.12	11.915	0.524	303.12	16.473	0.300
313.14	11.967	0.713	313.14	16.504	0.420
323.16	12.034	0.947	323.16	16.552	0.574
333.13	12.107	1.228	333.13	16.592	0.771
343.13	12.197	1.530	343.13	16.640	1.010
353.13	12.292	1.901	353.13	16.688	1.300
363.12	12.405	2.341	363.12	16.745	1.622
373.16	12.541	2.840	373.16	16.802	2.004
303.12	18.475	0.235			
313.14	18.532	0.336			
323.16	18.616	0.465			
333.13	18.701	0.626			
343.13	18.816	0.826			
353.13	18.951	1.066			
363.12	19.116	1.328			
373.16	19.314	1.620			

Table 2. Antoine's Equation Parameters

a_0	3.5950	b_0	$9.5779 \cdot 10^{2}$
a_1	$3.7340 \cdot 10^{-2}$	b_1	$1.1198 \cdot 10$
a_2	$-1.6123 \cdot 10^{-2}$	b_2	-4.0770
a_3	$1.4081 \cdot 10^{-3}$	b_3	$4.2411 \cdot 10^{-1}$
a_4	$-3.4826 \cdot 10^{-5}$	b_4	$-1.1176 \cdot 10^{-2}$

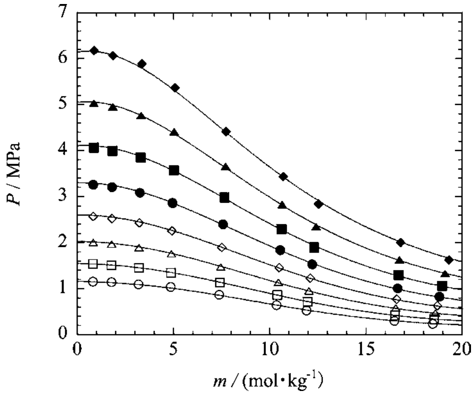

Figure 1. Comparison of the vapor pressure data for the NH_4I + NH_3 mixtures with results from Antoine's equation. ○, 303.12 K; □, 313.14 K; △, 323.16 K; ◇, 333.13 K; ●, 343.13 K; ■, 353.13 K; ▲, 363.12 K; ◆, 373.16 K; solid line indicates correlations.

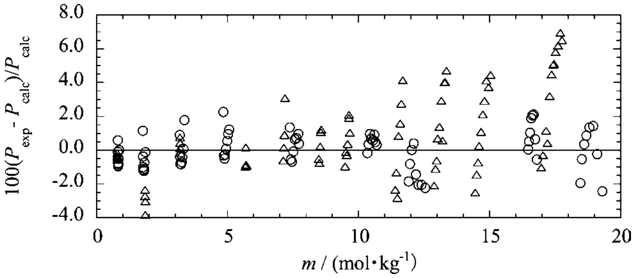

Figure 2. Deviations of experimental data from Antoine's equation. ○, this work; △, Yamamoto et al.[8]

the vapor phase should be as small as possible to reduce the effect of ambiguity of assumption 2.

The liquid densities of the NH_4I + NH_3 mixtures were measured with a glass piezometer, which has been described in detail elsewhere.[12] Weighed NH_4I is 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_4I in NH_3, the glass cell was inserted 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_4I + NH_3 Mixtures. The experimental results of the vapor pressures for NH_4I + NH_3 mixtures are given in Table 1. The vapor pressures were correlated with Antoine's equation. The Antoine constants were expressed as the fourth-degree function of molality.

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

$$A = \sum_{i}^{4} a_i (m/\text{mol·kg}^{-1})^i \qquad (2)$$

$$B = \sum_{i}^{4} b_i (m/\text{mol·kg}^{-1})^i \qquad (3)$$

$$C = 241.26 \qquad (4)$$

The values of these parameters were determined by using the present experimental results with a least-squares method and are listed in Table 2. Comparisons of the vapor pressure data for the NH_4I + NH_3 mixture with the results from Antoine's equation are shown in Figure 1. The Antoine equation correlated the experimental values of the NH_4I + NH_3 mixture within ± 2.5 %. Figure 2 shows the deviations of the experimental vapor pressure data in the literature[8] from the values calculated by eq 1 in our experimental range. The results of Yamamoto et al. are in good agreement with ours except for the high concentration range.

Liquid Density Measurement of NH_4I + NH_3 Mixtures. The experimental results of the liquid densities of the NH_4I + NH_3 mixture are shown in Table 3. The $P\rho Tm$ relations for the NH_4I + NH_3 mixture were correlated with the Tait equation.[13]

$$\frac{\rho/\text{kg·m}^{-3} - \rho_0/\text{kg·m}^{-3}}{\rho/\text{kg·m}^{-3}} = E \ln\left(\frac{D + P/\text{MPa}}{D + P_0}\right) \qquad (5)$$

where ρ and ρ_0 are the densities at P and P_0 (= 10.0 MPa), respectively. E and D are adjustable parameters. The parameters were optimized by minimizing the deviation of the calculated

Table 3. Experimental Results of the Liquid Densities of the NH_4I + NH_3 Mixtures

T	*m*	*P*	*ρ*	*T*	*m*	*P*	*ρ*
K	mol·kg^{-1}	MPa	kg·m^{-3}	K	mol·kg^{-1}	MPa	kg·m^{-3}
303.15	0.867	10.0	698	313.15	0.867	10.0	684
		15.0	702			15.0	688
		20.0	706			20.0	692
		25.0	710			25.0	696
		30.0	714			30.0	700
	1.827	10.0	777		1.827	10.0	763
		15.0	781			15.0	767
		20.0	784			20.0	771
		25.0	787			25.0	775
		30.0	791			30.0	779
	3.103	10.0	871		3.103	10.0	857
		15.0	874			15.0	861
		20.0	878			20.0	865
		25.0	881			25.0	868
		30.0	885			30.0	871
	4.856	10.0	988		4.856	10.0	975
		15.0	992			15.0	979
		20.0	996			20.0	982
		25.0	1000			25.0	986
		30.0	1004			30.0	990
	7.271	10.0	1109		7.271	10.0	1098
		15.0	1112			15.0	1101
		20.0	1115			20.0	1104
		25.0	1118			25.0	1107
		30.0	1120			30.0	1110
	11.181	10.0	1234		11.181	10.0	1223
		15.0	1237			15.0	1226
		20.0	1239			20.0	1229
		25.0	1241			25.0	1231
		30.0	1244			30.0	1234
	16.465	10.0	1330		16.465	10.0	1322
		15.0	1332			15.0	1324
		20.0	1335			20.0	1327
		25.0	1337			25.0	1329
		30.0	1339			30.0	1331
323.15	0.867	10.0	668	333.15	0.867	10.0	651
		15.0	673			15.0	656
		20.0	677			20.0	661
		25.0	681			25.0	666
		30.0	686			30.0	671
	1.827	10.0	749		1.827	10.0	733
		15.0	753			15.0	737
		20.0	757			20.0	741
		25.0	761			25.0	746
		30.0	765			30.0	750
	3.103	10.0	844		3.103	10.0	829
		15.0	848			15.0	834
		20.0	852			20.0	838
		25.0	856			25.0	842
		30.0	860			30.0	846
	4.856	10.0	961		4.856	10.0	948
		15.0	965			15.0	952
		20.0	969			20.0	956
		25.0	973			25.0	959
		30.0	977			30.0	963
	7.271	10.0	1086		7.271	10.0	1076
		15.0	1089			15.0	1079
		20.0	1093			20.0	1082
		25.0	1096			25.0	1085
		30.0	1099			30.0	1087
	11.181	10.0	1212		11.181	10.0	1200
		15.0	1215			15.0	1203
		20.0	1217			20.0	1206
		25.0	1219			25.0	1208
		30.0	1221			30.0	1210
	16.465	10.0	1312		16.465	10.0	1303
		15.0	1315			15.0	1305
		20.0	1317			20.0	1308
		25.0	1319			25.0	1310
		30.0	1322			30.0	1312
343.15	0.867	10.0	632	353.15	0.867	10.0	616
		15.0	638			15.0	622
		20.0	644			20.0	628
		25.0	649			25.0	634
		30.0	655			30.0	640
	1.827	10.0	716		1.827	10.0	700
		15.0	722			15.0	706
		20.0	727			20.0	711
		25.0	732			25.0	717
		30.0	737			30.0	722
	3.103	10.0	815		3.103	10.0	798
		15.0	819			15.0	803
		20.0	823			20.0	808
		25.0	828			25.0	814
		30.0	832			30.0	819
	4.856	10.0	933		4.856	10.0	918
		15.0	937			15.0	922
		20.0	941			20.0	927
		25.0	945			25.0	931
		30.0	949			30.0	935
	7.271	10.0	1062		7.271	10.0	1050
		15.0	1066			15.0	1054
		20.0	1069			20.0	1057
		25.0	1072			25.0	1060
		30.0	1075			30.0	1064
	11.181	10.0	1189		11.181	10.0	1178
		15.0	1192			15.0	1181
		20.0	1195			20.0	1184
		25.0	1197			25.0	1187
		30.0	1200			30.0	1189
	16.465	10.0	1293		16.465	10.0	1285
		15.0	1296			15.0	1287
		20.0	1299			20.0	1290
		25.0	1301			25.0	1292
		30.0	1304			30.0	1295
363.15	0.867	10.0	594	373.15	0.867	10.0	580
		15.0	602			15.0	587
		20.0	610			20.0	595
		25.0	617			25.0	603
		30.0	625			30.0	611
	1.827	10.0	680		1.827	10.0	667
		15.0	687			15.0	674
		20.0	694			20.0	681
		25.0	701			25.0	688
		30.0	708			30.0	695
	3.103	10.0	781		3.103	10.0	768
		15.0	786			15.0	774
		20.0	792			20.0	779
		25.0	797			25.0	785
		30.0	803			30.0	791
	4.856	10.0	903		4.856	10.0	900
		15.0	908			15.0	894
		20.0	913			20.0	899
		25.0	917			25.0	903
		30.0	921			30.0	908
	7.271	10.0	1037		7.271	10.0	1026
		15.0	1041			15.0	1030
		20.0	1044			20.0	1033
		25.0	1047			25.0	1037
		30.0	1051			30.0	1040
	11.181	10.0	1167		11.181	10.0	1155
		15.0	1170			15.0	1159
		20.0	1173			20.0	1162
		25.0	1176			25.0	1164
		30.0	1178			30.0	1167
	16.465	10.0	1275		16.465	10.0	1266
		15.0	1277			15.0	1269
		20.0	1280			20.0	1271
		25.0	1282			25.0	1273
		30.0	1284			30.0	1276

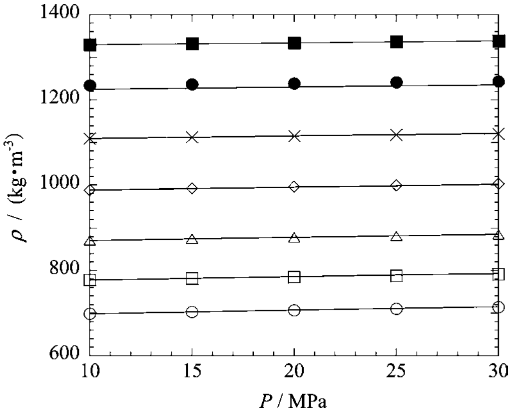

Figure 3. Comparison of the liquid density data for the $NH_4I + NH_3$ mixtures with results from the Tait form equation at 303.15 K. ○, $m = 0.867$; □, $m = 1.827$; △, $m = 3.103$; ◇, $m = 4.856$, ×, $m = 7.271$; ●, $m = 11.181$; ■, $m = 16.465$; solid line indicates correlations.

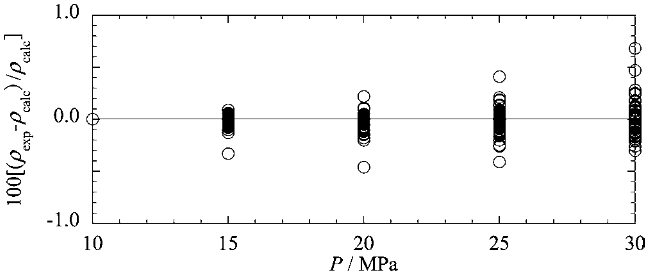

Figure 4. Deviations of the liquid density data from the Tait form equation.

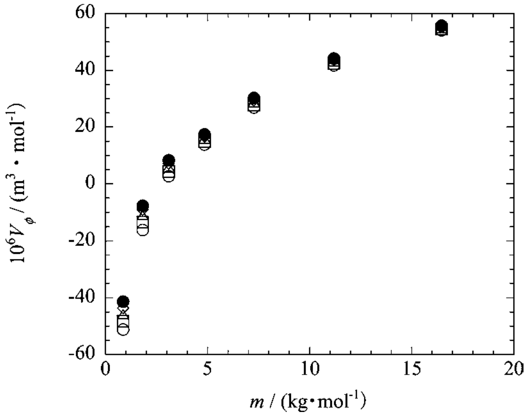

Figure 5. Molality dependence of the apparent molar volume of NH_4I in NH_3 at 303.15 K. ○, 10 MPa; □, 15 MPa; △, 20 MPa; ◇, 25 MPa; ●, 30 MPa.

density from the experimental one. For ammonia according to literature values,[14] E was equal to 0.09761, and D was expressed by a linear function of temperature as follows

$$D = 249.27 - 0.66019(T/\mathrm{K}) \tag{6}$$

For the $NH_4I + NH_3$ mixtures, E could be treated as a constant, 0.09761. The parameter D could be expressed by the following equation

$$D = D_0 + 16.42(m/\mathrm{mol{\cdot}kg^{-1}}) - 0.157(m/\mathrm{mol{\cdot}kg^{-1}})^2 \tag{7}$$

where D_0 is the value of D calculated from eq 6 and m is the molality. Comparisons of the liquid density data for the $NH_4I + NH_3$ mixtures with results from the Tait form equation at 303.15 K are shown in Figure 3. Figure 4 shows deviations of

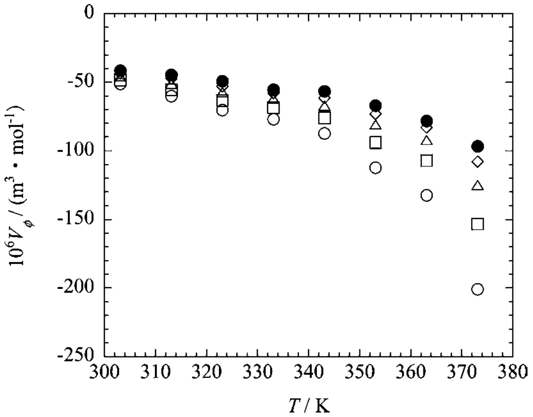

Figure 6. Temperature dependence of the apparent molar volume of NH_4I in NH_3 at $m = 0.867$. ○, 10 MPa; □, 15 MPa; △, 20 MPa; ◇, 25 MPa; ●, 30 MPa.

the experimental data from the Tait form equation. The Tait form equation correlated the experimental values of $NH_4I + NH_3$ mixtures is within 0.4 %.

The apparent molar volumes V_ϕ of NH_4I can be expressed as follows

$$V_\phi/(\mathrm{m^3{\cdot}mol^{-1}}) = \frac{(d°/(\mathrm{kg{\cdot}m^{-3}}) - d/(\mathrm{kg{\cdot}m^{-3}}))}{m/(\mathrm{mol{\cdot}kg^{-1}})d/(\mathrm{kg{\cdot}m^{-3}})d°/(\mathrm{kg{\cdot}m^{-3}})} + \frac{M}{1000(d/\mathrm{kg{\cdot}m^{-3}})} \tag{8}$$

where M is the molar mass of the NH_4I, m is the molality, d is the density of the solution, and $d°$ is the density of the NH_3. Literature values were used for the density of NH_3.[14] No literature values for the apparent molar volumes of NH_4I in NH_3 are available. Figure 5 shows the plot of the apparent molar volumes of NH_4I in NH_3 against molality at 303.15 K. The pressure dependence of the apparent molar volume decreased with increasing molality. Figure 6 shows the plot of the apparent molar volumes of NH_4I in NH_3 against temperature at $m = 1.143$. The pressure dependence of the apparent molar volume increased with increasing temperature.

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