

# Vapor Pressures and Liquid Densities of Ammonium Bromide + Ammonia Mixtures

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Vapor pressures and liquid densities for ammonium bromide (NH<sub>4</sub>Br) + ammonia (NH<sub>3</sub>) mixtures were measured over a wide range of temperatures and molalities. Vapor pressures of the NH<sub>4</sub>Br + NH<sub>3</sub> mixtures were measured at temperatures ranging from (303.12 to 373.16) K and molalities ranging up to 18.034 mol·kg<sup>-1</sup> of NH<sub>4</sub>Br. Vapor pressures were measured with a static method. The experimental values were correlated with Antoine's equation. Liquid densities of the NH<sub>4</sub>Br + NH<sub>3</sub> 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 15.171 mol·kg<sup>-1</sup> of NH<sub>4</sub>Br. 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 for the materials as a high-power and high frequency electronics device. Therefore, high quality and large diameter bulk GaN is required. Several methods have been proposed and tested for the GaN crystal growth.<sup>1–3</sup> The ammonothermal method which is a solvothermal method is one of the most promising techniques for achieving this purpose.<sup>2,4–6</sup> In the acidic ammonothermal method, ammonia and ammonium halide are used as solvent and mineralizer, respectively.<sup>6,7</sup> However, there are a 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.<sup>8</sup> They also reported the liquid densities of these solutions at saturated vapor pressure.<sup>9</sup> However, there are no literature values for liquid densities of these solutions above saturated vapor pressure.

In our previous study, we measured the vapor pressures and liquid densities of ammonium chloride + ammonia mixtures.<sup>10</sup> 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 bromide (NH<sub>4</sub>Br) + ammonia (NH<sub>3</sub>) were measured. Vapor pressures of the NH<sub>4</sub>Br + NH<sub>3</sub> mixtures were measured at temperatures ranging from (303.12 to 373.16) K and molalities ranging up to 18.034 mol·kg<sup>-1</sup> of NH<sub>4</sub>Br. Liquid densities of the NH<sub>4</sub>Br + NH<sub>3</sub> 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 15.171 mol·kg<sup>-1</sup> of NH<sub>4</sub>Br.

## Experimental Section

**Materials.** NH<sub>4</sub>Br which had minimum purities of 99.0 % was purchased from Wako Pure Chemical Industries. It was

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**Table 1. Experimental Results of the Vapor Pressures for the NH<sub>4</sub>Br + NH<sub>3</sub> Mixtures**

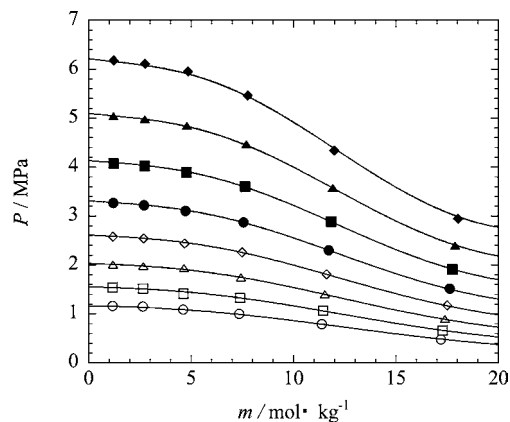
<i>T</i>	<i>m</i>	<i>P</i>	<i>T</i>	<i>m</i>	<i>P</i>
K	(mol·kg <sup>-1</sup> )	MPa	K	(mol·kg <sup>-1</sup> )	MPa
303.12	1.170	1.162	303.12	2.643	1.150
313.14	1.175	1.543	313.14	2.656	1.521
323.16	1.181	2.009	323.16	2.668	1.980
333.13	1.188	2.578	333.13	2.683	2.542
343.13	1.195	3.267	343.13	2.701	3.222
353.13	1.203	4.079	353.13	2.719	4.027
363.12	1.211	5.040	363.12	2.737	4.979
373.16	1.220	6.176	373.16	2.757	6.111
303.12	4.607	1.089	303.12	7.348	0.999
313.14	4.630	1.414	313.14	7.391	1.329
323.16	4.658	1.940	323.16	7.439	1.745
333.13	4.687	2.438	333.13	7.494	2.254
343.13	4.721	3.105	343.13	7.559	2.872
353.13	4.759	3.896	353.13	7.624	3.604
363.12	4.800	4.840	363.12	7.693	4.464
373.16	4.849	5.957	373.16	7.769	5.460
303.12	11.381	0.789	303.12	17.193	0.477
313.14	11.454	1.063	313.14	17.281	0.664
323.16	11.532	1.400	323.16	17.385	0.898
333.13	11.621	1.807	333.13	17.505	1.175
343.13	11.714	2.305	343.13	17.626	1.520
353.13	11.814	2.891	353.13	17.756	1.916
363.12	11.919	3.571	363.12	17.886	2.395
373.16	11.986	4.340	373.16	18.034	2.945

**Table 2. Antoine's Equation Parameters**

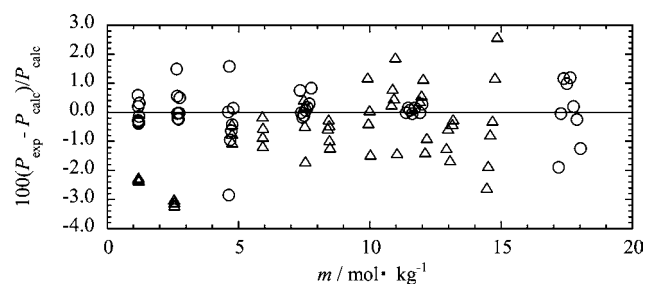
<i>a</i> <sub>0</sub>	3.7998	<i>b</i> <sub>0</sub>	1.0819·10 <sup>3</sup>
<i>a</i> <sub>1</sub>	-7.2179·10 <sup>-3</sup>	<i>b</i> <sub>1</sub>	-1.1810
<i>a</i> <sub>2</sub>	4.9158·10 <sup>-3</sup>	<i>b</i> <sub>2</sub>	1.5418
<i>a</i> <sub>3</sub>	-6.0406·10 <sup>-4</sup>	<i>b</i> <sub>3</sub>	-1.5073·10 <sup>-1</sup>
<i>a</i> <sub>4</sub>	2.0322·10 <sup>-5</sup>	<i>b</i> <sub>4</sub>	5.1599·10 <sup>-3</sup>

dried at 373.15 K for 12 h before measurement. The NH<sub>3</sub> of 99.999 % purity was supplied by Japan Fine Products Co. Ltd. The samples were used without further purification.

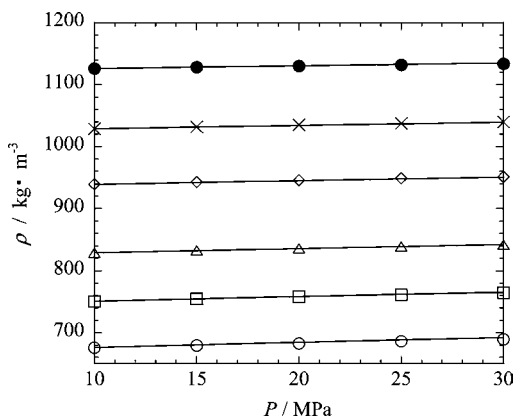
**Apparatus and Procedure.** The vapor pressure was measured with a static method. The experimental apparatus and procedures were the same as that described in our previous study.<sup>10</sup> Temperature and pressure values have an uncertainty of ± 0.02



**Figure 1.** Comparison of the vapor pressure data for the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures with results from Antoine's equation.  $\circ$ , 303.12 K;  $\square$ , 313.14 K;  $\triangle$ , 323.16 K;  $\diamond$ , 333.13 K;  $\bullet$ , 343.13 K;  $\blacksquare$ , 353.13 K;  $\blacktriangle$ , 363.12 K;  $\blacklozenge$ , 373.16 K; —, correlations.

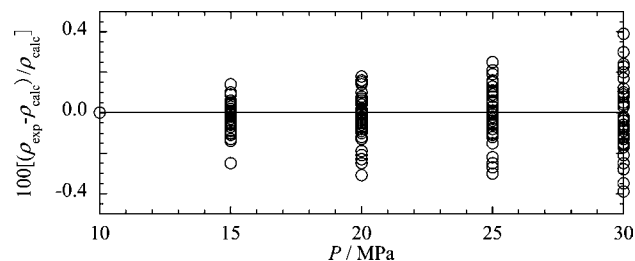


**Figure 2.** Deviations of experimental data from Antoine's equation.  $\circ$ , this work;  $\triangle$ , Yamamoto et al.<sup>8</sup>

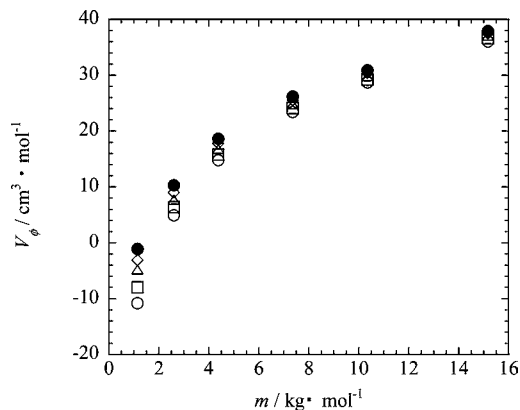


**Figure 3.** Comparison of the liquid density data for the ammonium bromide + ammonia mixture with results from the Tait-form equation at 303.15 K.  $\circ$ ,  $m = 1.143$ ;  $\square$ ,  $m = 2.601$ ;  $\triangle$ ,  $m = 4.381$ ;  $\diamond$ ,  $m = 7.359$ ;  $\times$ ,  $m = 10.349$ ;  $\bullet$ ,  $m = 15.171$ ; —, correlations.

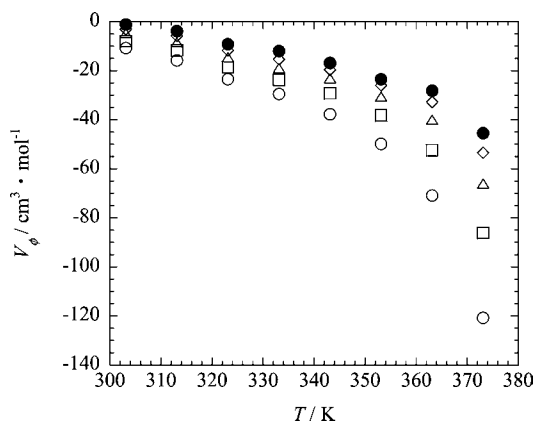
K and  $\pm 0.001$  MPa, respectively. The composition of the sample mixtures were determined by weighing. The uncertainty of the composition determination was estimated to be less than 0.05 wt %. On the basis of the uncertainties of these properties, the uncertainty of the vapor pressure data is estimated to be within  $\pm 0.5$  %. 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  $\text{NH}_4\text{Br}$  and stirring bar are charged in the cell. The valve and transducer were attached with the cell. After degassing for about 5 min, the  $\text{NH}_3$  was introduced into the cell with a plunger pump. The amount of  $\text{NH}_3$  charged in the cell was determined by weighing the cell with the electrical balance, accurate to within 0.01 g, before and after loading  $\text{NH}_3$ . After introducing  $\text{NH}_3$  and weighing the cell, the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixture was stirred with a magnetic



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



**Figure 5.** Molality dependence of apparent molar volume of  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$  at 303.15 K.  $\circ$ , 10 MPa;  $\square$ , 15 MPa;  $\triangle$ , 20 MPa;  $\diamond$ , 25 MPa;  $\bullet$ , 30 MPa.



**Figure 6.** Temperature dependence of apparent molar volume of  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$  at  $m = 1.143$ .  $\circ$ , 10 MPa;  $\square$ , 15 MPa;  $\triangle$ , 20 MPa;  $\diamond$ , 25 MPa;  $\bullet$ , 30 MPa.

stirring bar for 1 h to dissolve  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$ . 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. The concentration of the liquid mixture was determined as follows. The two assumptions were adopted: (1)  $\text{NH}_4\text{Br}$  does not exist in the vapor phase; (2) the vapor phase is ideal. The amounts of  $\text{NH}_4\text{Br}$  and  $\text{NH}_3$  and the volume of the cell were known experimentally. Therefore, if the density of the liquid mixture was known, we can evaluate the volumes of the vapor and liquid phase. Therefore, the concentration of the  $\text{NH}_4\text{Br}$  in the  $\text{NH}_3$  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).

The liquid densities of the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures were measured with a glass piezometer, which has been described

**Table 3. Experimental Results of the Liquid Densities of the NH<sub>4</sub>Br + NH<sub>3</sub> Mixtures**

<i>T</i>	<i>m</i>	<i>P</i>	$\rho$	<i>T</i>	<i>m</i>	<i>P</i>	$\rho$	<i>T</i>	<i>m</i>	<i>P</i>	$\rho$	<i>T</i>	<i>m</i>	<i>P</i>	$\rho$
K	(mol·kg <sup>-1</sup> )	MPa	(kg·m <sup>-3</sup> )	K	(mol·kg <sup>-1</sup> )	MPa	(kg·m <sup>-3</sup> )	K	(mol·kg <sup>-1</sup> )	MPa	(kg·m <sup>-3</sup> )	K	(mol·kg <sup>-1</sup> )	MPa	(kg·m <sup>-3</sup> )
303.15	1.143	10.0	675.9	313.15	1.143	10.0	661.3	343.15	1.143	10.0	612.8	353.15	1.143	10.0	594.5
		15.0	679.5			15.0	665.1			15.0	618.5			15.0	601.3
		20.0	682.7			20.0	668.9			20.0	624.1			20.0	607.9
		25.0	686.3			25.0	672.6			25.0	629.9			25.0	614.6
	2.601	30.0	689.5		30.0	676.3	30.0		635.4	30.0	621.2				
		10.0	750.8		2.601	10.0	737.8		2.601	10.0	693.7		2.601	10.0	676.6
		15.0	754.5			15.0	741.4			15.0	698.1			15.0	681.9
		20.0	758.0			20.0	745.0			20.0	702.6			20.0	687.1
		25.0	761.3			25.0	748.6			25.0	707.2			25.0	692.0
		30.0	764.4			30.0	752.1			30.0	711.7			30.0	697.0
	10.0	829.0	4.381			10.0	817.3			4.381	10.0			778.3	4.381
	15.0	832.7			15.0	820.9	15.0		782.6		15.0		769.6		
	20.0	836.1			20.0	824.2	20.0		786.7		20.0		773.8		
	25.0	839.1			25.0	827.6	25.0		790.7		25.0		778.1		
	30.0	842.1			30.0	830.7	30.0		794.2		30.0		782.2		
	10.0	939.1			7.359	10.0	926.8		7.359		10.0		891.2	7.359	
	15.0	942.7	15.0			929.8	15.0			894.7	15.0		882.5		
	20.0	945.8	20.0			932.8	20.0			898.2	20.0		886.2		
	25.0	948.9	25.0			935.5	25.0			901.6	25.0		889.7		
	30.0	951.2	30.0			938.0	30.0			904.9	30.0		893.2		
	10.0	1028.9	10.349			10.0	1017.0			10.349	10.0		983.9		10.349
	15.0	1032.2			15.0	1020.3	15.0		987.4		15.0		976.5		
	20.0	1034.9			20.0	1023.2	20.0		991.3		20.0		979.8		
	25.0	1037.4			25.0	1025.9	25.0		993.6		25.0		983.0		
	30.0	1039.8			30.0	1028.6	30.0		995.8		30.0		986.6		
	10.0	1126.2			15.171	10.0	1116.9		15.171		10.0		1086.6	15.171	
	15.0	1128.1	15.0			1118.8	15.0			1089.1	15.0		1080.1		
	20.0	1130.1	20.0			1120.4	20.0			1091.2	20.0		1082.2		
25.0	1132.0	25.0	1122.0	25.0		1093.3	25.0	1084.5							
30.0	1134.0	30.0	1123.6	30.0		1095.4	30.0	1086.3							
323.15	1.143	10.0	646.8	333.15		1.143	10.0	630.2		363.15	1.143	10.0	576.0		373.15
		15.0	651.2		15.0		635.4	15.0	583.7			15.0	569.5		
		20.0	655.4		20.0		640.3	20.0	590.9			20.0	577.4		
		25.0	659.7		25.0		645.1	25.0	598.2			25.0	585.2		
	2.601	30.0	663.8		30.0	649.5	30.0	605.2	30.0		592.7				
		10.0	724.3		2.601	10.0	709.5	2.601	10.0		659.3	2.601	10.0	646.4	
		15.0	727.7			15.0	714.0		15.0		665.4		15.0	652.4	
		20.0	731.4			20.0	718.3		20.0		671.2		20.0	658.4	
		25.0	734.9			25.0	722.5		25.0		677.1		25.0	664.3	
		30.0	738.7			30.0	726.3		30.0		682.6		30.0	670.0	
	10.0	805.0	4.381			10.0	791.1		4.381		10.0		748.7	4.381	
	15.0	808.9			15.0	795.1	15.0	754.3			15.0	742.9			
	20.0	812.6			20.0	799.1	20.0	759.5			20.0	748.0			
	25.0	816.1			25.0	803.0	25.0	764.4			25.0	752.9			
	30.0	819.4			30.0	807.1	30.0	769.0			30.0	757.6			
	10.0	914.3			7.359	10.0	903.1	7.359			10.0	866.4	7.359		
	15.0	917.4	15.0			906.7	15.0		870.2		15.0	858.5			
	20.0	920.3	20.0			909.8	20.0		873.8		20.0	862.2			
	25.0	923.0	25.0			912.7	25.0		877.4		25.0	865.9			
	30.0	926.0	30.0			915.6	30.0		881.3		30.0	870.0			
	10.0	1005.2	10.349			10.0	994.4		10.349		10.0	961.1		10.349	
	15.0	1008.3			15.0	997.8	15.0	965.6			15.0	954.3			
	20.0	1011.2			20.0	1001.2	20.0	969.0			20.0	958.0			
	25.0	1014.1			25.0	1004.0	25.0	972.5			25.0	961.3			
	30.0	1016.7			30.0	1006.9	30.0	975.7			30.0	964.7			
	10.0	1105.9			15.171	10.0	1096.0	15.171			10.0	1067.8	15.171		
	15.0	1107.8	15.0			1098.2	15.0		1070.1		15.0	1060.3			
	20.0	1109.7	20.0			1100.3	20.0		1072.4		20.0	1062.6			
25.0	1111.5	25.0	1102.2	25.0		1074.8	25.0		1065.1						
30.0	1113.4	30.0	1104.0	30.0		1076.8	30.0		1067.1						

in detail elsewhere.<sup>11</sup> Weighed NH<sub>4</sub>Br is charged in the glass cell, and the valve was attached with the glass cell. After degassing for about 5 min, NH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>. After dissolving NH<sub>4</sub>Br in NH<sub>3</sub>, the glass cell set

into the pressure vessel. The sample cell volume was approximately 13 cm<sup>3</sup>. The estimated uncertainties in the liquid densities are  $\pm 0.2\%$ .

## Results and Discussion

**Vapor Pressure Measurement of the NH<sub>4</sub>Br + NH<sub>3</sub> Mixtures.** The experimental results of the vapor pressures for the NH<sub>4</sub>Br + NH<sub>3</sub> 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.

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

$$A = \sum_{i=0}^4 a_i (m/\text{mol} \cdot \text{kg}^{-1})^i \quad (2)$$

$$B = \sum_{i=0}^4 b_i (m/\text{mol} \cdot \text{kg}^{-1})^i \quad (3)$$

$$C = 259.86 \quad (4)$$

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  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures with the results from Antoine's equation are shown in Figure 1. The Antoine equation correlated the experimental values of the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixture within  $\pm 2.9\%$ . Figure 2 shows the deviations of the experimental vapor pressure data in the literature<sup>8</sup> from the values calculated

**Table 4. Apparent Molar Volumes of  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$**

<i>T</i>	<i>m</i>	<i>P</i>	<i>V<sub>φ</sub></i>	<i>T</i>	<i>m</i>	<i>P</i>	<i>V<sub>φ</sub></i>	<i>T</i>	<i>m</i>	<i>P</i>	<i>V<sub>φ</sub></i>	<i>T</i>	<i>m</i>	<i>P</i>	<i>V<sub>φ</sub></i>		
K	(mol·kg <sup>-1</sup> )	MPa	(cm <sup>3</sup> ·mol <sup>-1</sup> )	K	(mol·kg <sup>-1</sup> )	MPa	(cm <sup>3</sup> ·mol <sup>-1</sup> )	K	(mol·kg <sup>-1</sup> )	MPa	(cm <sup>3</sup> ·mol <sup>-1</sup> )	K	(mol·kg <sup>-1</sup> )	MPa	(cm <sup>3</sup> ·mol <sup>-1</sup> )		
303.15	1.143	10.0	-10.8	313.15	1.143	10.0	-15.8	343.15	1.143	10.0	-37.8	353.15	1.143	10.0	-49.9		
		15.0	-8.0			15.0	-11.7			15.0	-29.2			15.0	-38.3		
		20.0	-4.8			20.0	-8.5			20.0	-23.1			20.0	-30.5		
		25.0	-3.1			25.0	-5.8			25.0	-19.6			25.0	-26.0		
	2.601	30.0	-1.1		30.0	-3.8	2.601		30.0	-16.8	2.601		30.0	-16.8	2.601	30.0	-23.5
		10.0	4.9		10.0	0.1			10.0	-19.3			10.0	-28.5			
		15.0	6.4		15.0	2.4			15.0	-13.4			15.0	-20.8			
		20.0	7.7		20.0	4.3			20.0	-9.0			20.0	-15.0			
		25.0	9.0		25.0	5.9			25.0	-5.6			25.0	-10.3			
		30.0	10.3		30.0	7.3			30.0	-2.8			30.0	-6.8			
	4.381	10.0	14.8		10.0	10.8	4.381		10.0	10.8	4.381		10.0	-5.4	4.381	10.0	-14.3
		15.0	15.8		15.0	12.3			15.0	-1.6			15.0	-8.7			
		20.0	16.8		20.0	13.7			20.0	1.5			20.0	-4.4			
		25.0	17.8		25.0	14.9			25.0	4.1			25.0	-1.0			
		30.0	18.6		30.0	16.0			30.0	6.5			30.0	1.9			
		10.0	23.4		10.0	21.0			7.359	10.0			9.5	7.359		10.0	3.8
	15.0	24.1	15.0		22.1	15.0	12.1			15.0	7.3						
	20.0	24.8	20.0		23.1	20.0	14.3			20.0	10.2						
	25.0	25.5	25.0		24.1	25.0	16.1			25.0	12.5						
	30.0	26.2	30.0		25.0	30.0	17.6			30.0	14.5						
	10.0	28.7	10.0		26.8	10.349	10.0			17.9	10.349		10.0		13.4		
	15.0	29.2	15.0		27.6		15.0		19.8	15.0			16.0				
	20.0	29.8	20.0		28.3		20.0		21.2	20.0			18.1				
	25.0	30.4	25.0		29.0		25.0		22.8	25.0			19.9				
30.0	30.9	30.0	29.6	30.0	24.1		30.0	21.3									
10.0	36.0	10.0	34.5	15.171	10.0		28.1	15.171	10.0	24.7							
15.0	36.6	15.0	35.1		15.0	29.5	15.0		26.7								
20.0	37.1	20.0	35.8		20.0	30.7	20.0		28.3								
25.0	37.5	25.0	36.4		25.0	31.8	25.0		29.6								
30.0	37.9	30.0	37.0		30.0	32.7	30.0		30.8								
323.15	1.143	10.0	-23.5		333.15	1.143	10.0		-29.5	363.15	1.143	10.0	-70.9	373.15	1.143	10.0	-120.8
		15.0	-18.6	15.0			-23.7	15.0	-52.4			15.0	-86.2				
		20.0	-14.5	20.0			-18.9	20.0	-40.0			20.0	-66.0				
		25.0	-11.7	25.0			-15.3	25.0	-32.8			25.0	-53.5				
	2.601	30.0	-9.2	30.0		-11.9	2.601	30.0	-11.9		2.601	30.0	-28.1		2.601	30.0	-45.4
		10.0	-5.7	10.0		-11.8		10.0	-42.2			10.0	-68.7				
		15.0	-2.1	15.0		-8.0		15.0	-31.0			15.0	-49.7				
		20.0	0.5	20.0		-4.8		20.0	-22.8			20.0	-37.2				
		25.0	2.9	25.0		-2.2		25.0	-17.1			25.0	-28.4				
		30.0	4.6	30.0		0.4		30.0	-12.4			30.0	-21.7				
	4.381	10.0	6.3	10.0		1.5	4.381	10.0	-24.0		4.381	10.0	-41.9				
		15.0	8.3	15.0		4.2		15.0	-16.5			15.0	-29.6				
		20.0	10.0	20.0		6.5		20.0	-11.0			20.0	-21.2				
		25.0	11.6	25.0		8.4		25.0	-6.6			25.0	-14.9				
		30.0	13.0	30.0		9.9		30.0	-3.0			30.0	-10.0				
		10.0	18.1	10.0		14.2		7.359	10.0			-3.9	7.359		10.0	-14.7	
	15.0	19.6	15.0	16.0		15.0	1.3		15.0		-6.8						
	20.0	20.9	20.0	17.7		20.0	5.2		20.0		-1.2						
	25.0	22.1	25.0	19.2		25.0	8.4		25.0		3.1						
	30.0	23.1	30.0	20.5		30.0	10.9		30.0		6.4						
	10.0	24.5	10.0	21.6		10.349	10.0		7.7		10.349	10.0			-0.3		
	15.0	25.6	15.0	23.0			15.0	11.3	15.0			5.3					
	20.0	26.6	20.0	24.1			20.0	14.2	20.0			9.4					
	25.0	27.4	25.0	25.2			25.0	16.5	25.0			12.5					
30.0	28.2	30.0	26.2	30.0	18.4		30.0	15.0									
10.0	32.8	10.0	30.7	15.171	10.0		20.6	15.171	10.0	15.0							
15.0	33.7	15.0	31.8		15.0	23.3	15.0		19.0								
20.0	34.5	20.0	32.8		20.0	25.5	20.0		22.0								
25.0	35.2	25.0	33.7		25.0	27.2	25.0		24.3								
30.0	35.8	30.0	34.4		30.0	28.7	30.0		26.2								

by eq 1 in our experimental range. The results of Yamamoto et al. are in good agreement with ours.

**Liquid Density Measurement of the  $\text{NH}_4\text{Br} + \text{NH}_3$  Mixtures.** The experimental results of the liquid densities of the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures are shown in Table 3. The  $P\rho Tm$  relations for the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures were correlated with the Tait equation.<sup>12</sup>

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

where  $\rho$  and  $\rho_0$  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 density from the experimental one. For ammonia according to literature values,<sup>13</sup>  $E$  was equal to 0.09761 and  $D$  was expressed by a linear function of temperature as follows

$$D = 249.27 - 0.66019T/\text{K} \quad (6)$$

For the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures,  $E$  could be treated as a constant, 0.09761. The parameter  $D$  could be expressed by the following equation

$$D = D_0 + 12.50m/\text{mol} \cdot \text{kg}^{-1} - 0.038(m/\text{mol} \cdot \text{kg}^{-1})^2 \quad (7)$$

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  $\text{NH}_4\text{Br} + \text{NH}_3$  mixture with results from the Tait-form equation at 303.15 K are shown in Figure 3. Figure 4 shows deviations of the experimental data from the Tait-form equation. The Tait-form equation correlated the experimental values of the  $\text{NH}_4\text{Br} + \text{NH}_3$  mixtures within 0.4 %.

The apparent molar volumes  $V_\phi$  of  $\text{NH}_4\text{Br}$  can be expressed as follows

$$V_\phi/\text{cm}^3 \cdot \text{mol}^{-1} = \frac{1000(d^\circ/\text{g} \cdot \text{cm}^{-3} - d/\text{g} \cdot \text{cm}^{-3})}{m/\text{mol} \cdot \text{kg}^{-1}d/\text{g} \cdot \text{cm}^{-3}d^\circ/\text{g} \cdot \text{cm}^{-3}} + \frac{M}{d/\text{g} \cdot \text{cm}^{-3}} \quad (8)$$

where  $M$  is the molecular weight of the  $\text{NH}_4\text{Br}$ ;  $m$  is the molality;  $d$  is the density of the solution; and  $d^\circ$  is the density of the  $\text{NH}_3$ . Literature values were used for the density of  $\text{NH}_3$ .<sup>13</sup> Table 4 shows the apparent molar volumes of  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$ . No literature values for the apparent molar volumes of  $\text{NH}_4\text{Br}$

in  $\text{NH}_3$  are available. Figure 5 shows the plot of the apparent molar volumes of  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$  against molality at 303.15 K. The pressure of the apparent molar volume decreased with increasing molality. Figure 6 shows the plot of the apparent molar volumes of  $\text{NH}_4\text{Br}$  in  $\text{NH}_3$  against temperature at  $m = 1.143 \text{ mol} \cdot \text{kg}^{-1}$ . The pressure dependence of the apparent molar volume increased with increasing temperature.

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