

The $pVTx$ Properties of Aqueous Solutions of Ammonia in the Range of Around 50 mol% of Ammonia

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For preliminary comparisons in the range of compositions of about 50 mol% NH₃, an experimental study of the pressure-volume-temperature-composition ($pVTx$) properties for aqueous solutions of ammonia has been conducted by using a constant-volume apparatus in the range of temperatures from 297 to 309 K, densities from 810 to 823 kg·m⁻³, and of pressures up to 15 MPa. And these new data have been compared with available experimental data measured by Harms-Watzenberg [1], and Munakata et al. [2], and with the equation of state of this system correlated by Tillner-Roth and Friend [3].

1. Introduction

The aqueous solution of ammonia has been used not only for absorption refrigerators but also for waste heat recovery from power generation systems and other purposes. Then, the thermodynamic and transport properties of NH₃-H₂O mixtures are needed over a wide range of state parameters.

Experimental studies of $pVTx$ properties for this system have been conducted concerning the vapor-liquid equilibrium since 1901, and, in the single phase, $pVTx$ property measurements have been made since 1920.

Tillner-Roth and Friend [3] have developed an equation of state for NH₃-H₂O mixtures, based on measured data mainly by Harms-Watzenberg [1].

In the above investigations of thermodynamic properties, however, any experimental data have not expressed the maximum density behavior. Then authors have precisely measured the $pVTx$ property data in the maximum density region for the range of compositions below 10 mol% of ammonia [4].

In the present paper, for the preliminary confirmation of uncertainties of the equation of state by Tillner-Roth and Friend [3], new measurements of $pVTx$ properties have been made in the range of compositions around 50 mol% of ammonia.

2. Survey of Previous Experimental Studies of $pVTx$ Properties near 50 mol% NH₃

The available $pVTx$ property data for liquid NH₃-H₂O mixtures in the composition range of about 0.5

mole fraction NH₃ cover the temperature range of 243 to 413 K, the pressure range up to 37.58 MPa, and the density range of 695 to 884 kg·m⁻³, measured by Harms-Watzenberg [1], and Munakata et al. [2].

Harms-Watzenberg [1] obtained 290 data points in the range of temperatures from 243 to 413 K, pressures from 0.8 to 37.58 MPa, densities from 695 to 884 kg·m⁻³, and a composition of 0.50321 mole fraction NH₃.

Munakata et al. [2] obtained 299 data points in the range of temperatures from 310 to 400 K, pressures from 0.7 to 17 MPa, densities from 714 to 828 kg·m⁻³, and a composition of 0.5052 mole fraction NH₃.

Kondo et al. [5] obtained 140 data points in the range of temperatures from 310 to 400 K, pressures from 0.8 to 17 MPa, densities from 667 to 791 kg·m⁻³, and a composition of 0.6005 mole fraction NH₃. In this paper, their data were not adopted for comparisons because of the difference of mole fractions.

3. Experimental Method

A constant-volume apparatus [6] with a cylindrical piezometer with an inner volume of approximately 245 cm³ has been used for the present measurements of $pVTx$ properties in the range of temperatures from 298 to 309 K, pressures up to 15.6 MPa, densities from 810 to 823 kg·m⁻³, and compositions of 0.5133 and 0.5357 mole fractions of ammonia. The temperature was

measured within 7 mK with the use of a platinum resistance thermometer calibrated within 2 mK by the National Physical Laboratory in the United Kingdom, based on the International Temperature Scale (1990). The pressure was measured within 5 kPa with a quartz Bourdon-type digital pressure gauge, RUSKA series 6000 calibrated against an air piston gauge. The density was determined within 0.01% by means of dividing the mass of the sample by the entire inner volume of the piezometer, taking into account the deformation effects by temperature and pressure. The composition was calculated within 0.01 mol% from each charged mass of water and ammonia while filling the piezometer.

The inner volume of the cylindrical piezometer was calibrated with the use of the distilled ordinary water density calculated from the IAPWS-1995 Formulation [7]. And the measured water densities were compared with the experimental results by Kell [8], and agreed with Kell's data within 0.002% and with the IAPWS-1995 Formulation within 0.004%.

4. Results

In the previous paper [4], authors presented that the equation of state developed by Tillner-Roth and Friend has not expressed the $pVTx$ property data in the maximum density region for the range of compositions below 10 mol% of ammonia [4]. Then, for confirmation of them [4], the $pVTx$ properties of $\text{NH}_3\text{-H}_2\text{O}$ mixtures have been measured by using the same apparatus in the range of compositions of about 50 mol% NH_3 .

Measurements of the $pVTx$ properties of $\text{NH}_3\text{-H}_2\text{O}$ mixtures were made in the range of temperatures from 298 to 309 K, pressures from 0.5 to 15.7 MPa, densities of about 810 and 823 $\text{kg}\cdot\text{m}^{-3}$ and compositions of 0.5133 and 0.5357 mole fractions of ammonia as shown in Table 1.

5. Discussion and Conclusion

The experimental $pVTx$ properties of $\text{NH}_3\text{-H}_2\text{O}$ mixtures in a limited range listed in Table 1 were compared with the equation of state developed by Tillner-Roth and Friend [3].

The deviations of these measured densities from the equation of state are plotted against temperature in Fig. 1 for the composition of 0.5133 mole fraction NH_3 , and in Fig. 2 for 0.5357 mole fraction NH_3 .

Table 1. Experimental results of the $pVTx$ properties of $\text{NH}_3\text{-H}_2\text{O}$ mixtures in the range of densities of about 810 and 823 $\text{kg}\cdot\text{m}^{-3}$ and compositions of 0.5123 and 0.5357 mole fractions of ammonia.

Temp. /K	Pressure /MPa	Density / $\text{kg}\cdot\text{m}^{-3}$	Mole Fraction of NH_3
297.750	0.8222	823.38	0.5133
298.151	1.3775	823.34	0.5133
299.151	3.0541	823.22	0.5133
300.151	5.0155	823.10	0.5133
301.150	7.0086	822.97	0.5133
301.151	7.0096	822.97	0.5133
303.149	11.0087	822.72	0.5133
305.151	15.0152	822.47	0.5133
301.539	0.5210	811.59	0.5357
302.152	1.6271	811.52	0.5357
303.151	3.6268	811.39	0.5357
304.151	5.6192	811.26	0.5357
305.151	7.6308	811.14	0.5357
307.153	11.6528	810.89	0.5357
309.151	15.6551	810.65	0.5357

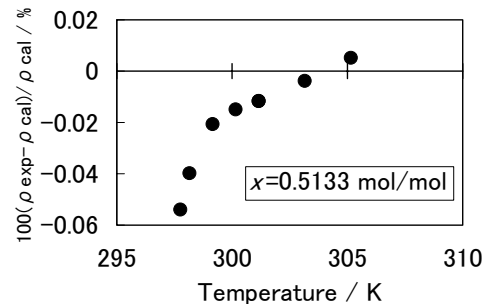


Fig. 1. Deviation of measured densities from equation of state by Tillner-Roth and Friend [3] along 823 $\text{kg}\cdot\text{m}^{-3}$ and 0.5133 mol/mol.

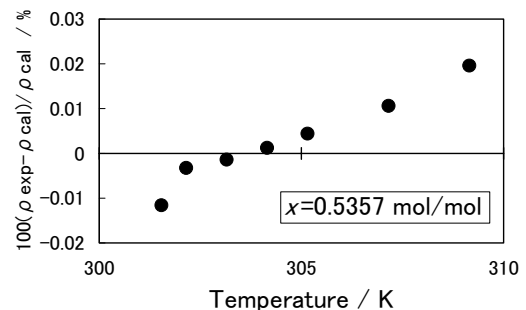


Fig. 2. Deviation of measured densities from equation of state by Tillner-Roth and Friend [3] along 811 $\text{kg}\cdot\text{m}^{-3}$ and 0.5357 mol/mol.

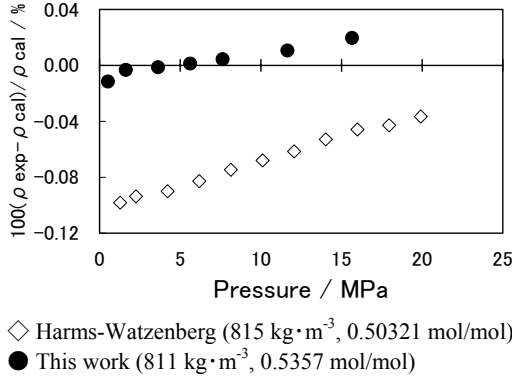


Fig. 3. Deviations of Harms-Watzenberg [1] and this work from equation of state by Tillner-Roth and Friend [3] along about $811 \text{ kg}\cdot\text{m}^{-3}$.

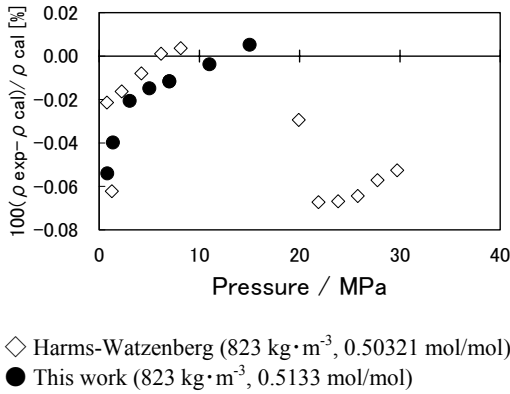


Fig. 4. Deviations of Harms-Watzenberg [1] and this work from equation of state by Tillner-Roth and Friend [3] along about $823 \text{ kg}\cdot\text{m}^{-3}$.

From the deviation plots of densities shown in Fig. 1 and Fig. 2, the measured data shown in Table 1 agree well within $\pm 0.06 \%$ with the equation of state by Tillner-Roth and Friend [3].

The measured data shown in Table 1 were plotted against pressure and compared with the data by Harms-Watzenberg [1] in Fig. 3 and Fig. 4, with the aid of the deviation plots from the equation of state by Tillner-Roth and Friend [3].

Two sets of experimental data by Harms-Watzenberg [1] and this work agree well within about $\pm 0.1 \%$ in such densities and compositions as shown in Fig. 3 and Fig. 4.

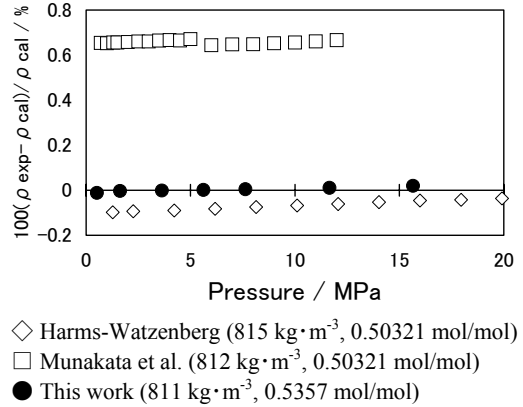


Fig. 5. Deviations of Harms-Watzenberg [1], Munakata et al. [2] and this work from equation of state by Tillner-Roth and Friend [3] along about $811 \text{ kg}\cdot\text{m}^{-3}$.

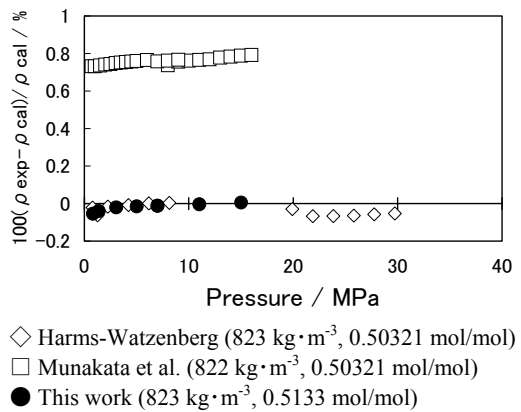


Fig. 6. Deviations of Harms-Watzenberg [1], Munakata et al. [2] and this work from equation of state by Tillner-Roth and Friend [3] along about $823 \text{ kg}\cdot\text{m}^{-3}$.

Finally three sets of experimental data by Harms-Watzenberg [1], Munakata et al. [2] and this work were compared with each other by comparing them with the equation of state by Tillner-Roth and Friend [3] as shown in Fig. 5 and Fig. 6.

The deviations of measured densities by Munakata et al. [2] are 0.6 to 0.8 % from the experimental data by Harms-Watzenberg [1], and this work, and also from the equation of state by Tillner-Roth and Friend [3], as shown in Fig. 5 and Fig. 6.

From above comparisons, it is concluded that the present experimental results are precise enough and agree with the equation of state developed by Tillner-Roth and Friend [3] in the range of compositions near 50 % mole fraction NH_3 .

Acknowledgments

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