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An Experimental Study of the $pVTx$ Properties for Aqueous Solutions of Ammonia Focusing on the Maximum Density Region[1]

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An experimental study of the pressure–volume–temperature-composition ($pVTx$) properties for the aqueous solution of ammonia, namely NH_3–H_2O mixtures, has been conducted with the use of a constant-volume apparatus, especially focusing on the maximum density behavior, in the range of temperatures from 253 to 309 K, pressures from 0.47 to 16.93 MPa, densities from 950 to 1007 $kg \cdot m^{-3}$ and compositions from 0 to 0.1436 mole fraction of ammonia. The behavior of the maximum densities for the aqueous solution of ammonia has been investigated for the first time by the present experimental study, and the available equations of state do not represent the $pVTx$ properties of the present measured data adequately near the maximum density region.

KEY WORDS: aqueous solution of ammonia; experimental data; maximum density; $pVTx$ properties.

1. INTRODUCTION

The aqueous solution of ammonia has been used not only for refrigeration cycles but also for waste heat recovery power systems and other purposes. Thus, the thermodynamic and transport properties of NH_3–H_2O mixtures over a wide range of state parameters are needed.

Experimental studies of $pVTx$ properties at the vapor–liquid equilibrium have been conducted since 1901, and, in the single phase, $pVTx$

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property measurements were made since 1920. Tillner-Roth and Friend [1] have developed an equation of state for NH_3–H_2O mixtures, based on measured data mainly by Harms-Watzenberg [2]. However, no data near the maximum density locus are available. Therefore, in the present paper, the maximum density behavior for NH_3–H_2O mixtures is experimentally investigated.

2. SURVEY OF PREVIOUS EXPERIMENTAL STUDIES OF *pVTx* PROPERTIES

The available *pVTx* property data for NH_3–H_2O mixtures in the single phase cover the temperature range of 243 to 520 K, the pressure range up to 48 MPa, the density range of 0.08 to 980 $kg \cdot m^{-3}$, and the composition range of 0.1 to 0.9 mole fraction NH_3. Neuhausen [3] measured 31 data points in the range of temperatures from 273 to 313 K, pressures from 0.1 to 0.5 MPa, densities from 0.8 to 0.9 $kg \cdot m^{-3}$, and compositions from 0.25 to 0.67 mole fraction NH_3. Harms-Watzenberg [2] obtained 1208 data points in the range of temperatures from 243 to 413 K, pressures from 0.8 to 38 MPa, densities from 425 to 980 $kg \cdot m^{-3}$, and compositions from 0.1 to 0.9 mole fraction NH_3, and also measured 276 data points in the range of temperatures from 373 to 498 K, pressures from 0.02 to 48 MPa, densities from 0.08 to 25.3 $kg \cdot m^{-3}$, and compositions from 0.25 to 0.75 mole fraction NH_3. Magee and Kagawa [4] obtained 355 data points in the range of temperatures from 300 to 520 K, pressures from 3.0 to 19.93 MPa, densities from 96 to 735 $kg \cdot m^{-3}$, and compositions from 0.71 to 0.90 mole fraction NH_3.

3. EXPERIMENTAL METHOD

A constant-volume apparatus [5] with a cylindrical piezometer with an inner volume of approximately 245 cm^3 has been used for the present measurements of *pVTx* properties in the range of temperatures from 253 to 309 K, pressures from 0.47 to 16.93 MPa, densities from 950 to 1007 $kg \cdot m^{-3}$, and compositions from 0 to 0.1436 mole fraction of ammonia. The temperature was measured within 5 mK, taking into account a temperature fluctuation of 2 mK against measuring time and position in a thermostated bath, 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 gage, Ruska Series 6000 calibrated with an air piston gage. The density was determined within 0.01% by means of dividing the mass

of the sample by the inner volume of the piezometer, taking into account the deformation effects of temperature and pressure. The composition was calculated within 0.01 mass% from each charged mass of water and ammonia while filling the piezometer.

The inner volume of the cylindrical piezometer was calibrated, for obtaining the average inner and outer diameters of this piezometer at 273.15 K, at seven state points in the range of temperatures from 298 to 313 K and pressures up to 17 MPa with the use of the distilled ordinary water density calculated from the IAPWS-1995 Formulation [6]. And the measured water densities were compared with the experimental results by Kell [7], and agreed with Kell's data within 0.002% and with the IAPWS-1995 Formulation within 0.004%.

The double-distilled ordinary water of electric resistivity above $600\,\mathrm{M}\,\Omega\cdot\mathrm{m}^{-1}$ was used for the sample, and the purity of ammonia was 99.999 mol% with impurities of O_2 below 2 ppm, N_2 below 5 ppm, CH_4 below 1 ppm, and H_2O below 2 ppm.

4. RESULTS

Measurements of the *pVTx* properties of NH_3–H_2O mixtures were made for dilute mixtures of ammonia including ordinary water substance in the range of temperatures from 253 to 309 K, pressures from 0.47 to 16.93 MPa, densities from 950 to $1007\,\mathrm{kg}\cdot\mathrm{m}^{-3}$ and compositions from 0 to 0.1436 mole fraction of ammonia as shown in Table I.

5. DISCUSSION AND CONCLUSION

The maximum density behavior for the aqueous solution of ammonia was experimentally investigated for the first time by the present measurements. The state of a minimum pressure along an isochore corresponds to the state of a maximum density, namely a minimum volume, along an isobar. Therefore, in Table I, the measured data along each isochore in the range of compositions from 0 to 0.0955 mole fraction NH_3 show a possibility of a minimum pressure in the low temperature region.

Figure 1 shows deviation plots of the measured *pVT* property data of ordinary water substance from IAPWS -1995 Formulation [6], and Fig. 2 shows a comparison of the measured *pVTx* property data of an aqueous solution of ammonia with the mixture equation of state, solid lines in Fig. 2, correlated by Tillner-Roth and Friend [1].

The present results of ordinary water substance agree well with the IAPWS-1995 Formulation, as shown in Fig. 1. From Fig. 2, the equation

Table I. Experimental Results of $pVTx$ Properties of Aqueous Solution of Ammonia

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.0000	274.120	13.4368	1006.525
0.0000	275.180	13.3549	1006.481
0.0000	276.176	13.3050	1006.440
0.0000	276.156	13.3064	1006.440
0.0000	277.161	13.2816	1006.397
0.0000	278.161	13.2882	1006.352
0.0000	279.166	13.3285	1006.305
0.0000	280.166	13.3736	1006.258
0.0000	281.174	13.4560	1006.209
0.0000	282.135	13.5621	1006.161
0.0000	283.180	13.6652	1006.109
0.0000	285.140	13.9942	1006.006
0.0000	288.147	14.7141	1005.837
0.0000	272.041	5.2190	1002.298
0.0000	273.150	5.0096	1002.262
0.0000	274.150	4.8435	1002.229
0.0000	275.146	4.7165	1002.192
0.0000	276.123	4.6144	1002.156
0.0000	277.150	4.5353	1002.115
0.0000	278.129	4.4908	1002.075
0.0000	279.103	4.4684	1002.033
0.0000	280.101	4.4691	1001.990
0.0000	281.139	4.5090	1001.939
0.0000	283.153	4.6495	1001.841
0.0000	286.052	5.0387	1001.687
0.0000	289.170	5.6776	1001.507
0.0000	292.123	6.5056	1001.325
0.0000	296.128	7.9388	1001.060
0.0000	300.129	9.7148	1000.779
0.0000	305.191	12.4237	1000.408
0.0000	308.160	14.2340	1000.186
0.0000	270.152	4.0742	1001.546
0.0000	271.167	3.8186	1001.517
0.0000	272.127	3.5966	1001.489
0.0000	273.099	3.4021	1001.459
0.0000	274.153	3.2201	1001.425
0.0000	275.163	3.0745	1001.389
0.0000	276.166	2.9604	1001.353
0.0000	277.151	2.8758	1001.315
0.0000	278.156	2.8198	1001.274
0.0000	279.164	2.7903	1001.231
0.0000	281.077	2.8076	1001.145

Table I. (*Continued*)

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.0140	271.150	3.9604	996.21
0.0140	272.151	3.7787	996.18
0.0140	273.150	3.6342	996.14
0.0140	273.150	3.6336	996.14
0.0140	275.150	3.4312	996.07
0.0140	275.150	3.4304	996.07
0.0140	277.150	3.3357	995.99
0.0140	279.150	3.3485	995.90
0.0140	281.150	3.4727	995.80
0.0140	283.150	3.6923	995.70
0.0140	285.150	4.0118	995.59
0.0140	287.150	4.4343	995.47
0.0140	289.150	4.9466	995.35
0.0140	291.150	5.5612	995.22
0.0140	293.150	6.2476	995.09
0.0140	295.150	7.0350	994.95
0.0140	297.150	7.9099	994.81
0.0140	299.150	8.8412	994.66
0.0140	301.150	9.8803	994.51
0.0140	303.150	10.9194	994.37
0.0140	305.150	12.1072	994.21
0.0140	309.150	14.6844	993.90
0.0302	270.144	4.3468	991.12
0.0302	271.170	4.2082	991.09
0.0302	272.150	4.1135	991.05
0.0302	273.137	4.0403	991.01
0.0302	274.154	3.9922	990.97
0.0302	275.153	3.9702	990.93
0.0302	277.149	4.0080	990.84
0.0302	279.146	4.1508	990.74
0.0302	281.151	4.3925	990.64
0.0302	283.151	4.7318	990.53
0.0302	285.146	5.1711	990.41
0.0302	289.148	6.3177	990.16
0.0302	292.142	7.4077	989.96
0.0302	292.146	7.4291	989.96
0.0302	295.107	8.6962	989.75
0.0302	298.159	10.2323	989.53
0.0470	266.119	16.2227	989.78
0.0470	267.146	16.0333	989.74
0.0470	268.165	15.9477	989.70
0.0470	269.168	15.8917	989.66
0.0470	270.132	15.8617	989.62

Table I. (*Continued*)

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.0470	270.148	15.8616	989.62
0.0470	271.110	15.8563	989.57
0.0470	271.134	15.8573	989.57
0.0470	272.153	15.8791	989.53
0.0470	273.166	15.9275	989.48
0.0470	274.142	15.9995	989.44
0.0470	275.159	16.0978	989.39
0.0513	268.099	7.3164	984.85
0.0513	269.097	7.2567	984.81
0.0513	269.102	7.2441	984.81
0.0513	270.152	7.1951	984.77
0.0513	271.150	7.1772	984.72
0.0513	272.148	7.1857	984.68
0.0513	273.150	7.2194	984.63
0.0513	274.150	7.2795	984.59
0.0513	275.152	7.3622	984.54
0.0513	277.151	7.6043	984.44
0.0513	279.149	7.9455	984.33
0.0513	281.150	8.3712	984.22
0.0513	283.150	8.8795	984.10
0.0513	285.150	9.5270	983.98
0.0513	287.151	10.2233	983.85
0.0513	289.150	11.0197	983.72
0.0513	291.150	11.8839	983.58
0.0513	295.149	13.8514	983.31
0.0582	266.151	2.6190	979.80
0.0582	267.133	2.4955	979.77
0.0582	268.174	2.4157	979.73
0.0582	269.189	2.3641	979.69
0.0582	271.177	2.3397	979.60
0.0582	273.146	2.4312	979.51
0.0582	275.143	2.6128	979.41
0.0582	279.142	3.2597	979.20
0.0582	283.122	4.2751	978.96
0.0582	287.131	5.7353	978.69
0.0582	289.136	6.5527	978.56
0.0582	291.127	7.4453	978.41
0.0582	293.140	8.4236	978.27
0.0582	295.119	9.4372	978.12
0.0582	297.148	10.5759	977.97
0.0582	299.080	11.7294	977.83
0.0582	303.201	14.3571	977.51
0.0582	305.214	15.7743	977.35
0.0591	265.619	0.8119	975.65

Table I. (*Continued*)

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.0591	266.139	0.7453	975.64
0.0591	266.626	0.6981	975.62
0.0591	267.158	0.6347	975.60
0.0591	269.109	0.5006	975.52
0.0591	271.122	0.4675	975.44
0.0591	273.143	0.5066	975.35
0.0591	275.133	0.6775	975.25
0.0591	277.184	0.9532	975.15
0.0591	281.222	1.7959	974.91
0.0591	285.172	2.9997	974.66
0.0591	289.044	4.4991	974.40
0.0591	293.221	6.4539	974.10
0.0591	297.220	8.6371	973.79
0.0591	301.020	10.9498	973.50
0.0591	305.109	13.7458	973.17
0.0606	263.965	16.2197	987.12
0.0606	265.002	16.1171	987.08
0.0606	265.992	16.0545	987.04
0.0606	268.025	15.9737	986.96
0.0606	268.996	15.9794	986.92
0.0606	270.988	16.0616	986.82
0.0606	273.143	16.2628	986.71
0.0606	274.993	16.5473	986.61
0.0606	277.145	16.9263	986.49
0.0640	265.384	8.3346	980.35
0.0640	266.145	8.2770	980.32
0.0640	267.142	8.2215	980.28
0.0640	269.149	8.1926	980.19
0.0640	269.151	8.1947	980.19
0.0640	271.151	8.2659	980.10
0.0640	273.151	8.4359	980.01
0.0640	275.148	8.7028	979.90
0.0640	277.142	9.0541	979.80
0.0640	279.171	9.5254	979.68
0.0640	281.130	10.0652	979.57
0.0640	281.186	10.1079	979.56
0.0640	283.153	10.7065	979.44
0.0640	285.163	11.4351	979.32
0.0640	287.129	12.2059	979.19
0.0640	289.150	13.1141	979.06
0.0640	291.150	14.0802	978.92
0.0640	293.156	15.1122	978.78
0.0644	265.183	5.3119	979.94
0.0644	267.169	5.1937	979.87

Table I. (*Continued*)

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.0644	269.145	5.1799	979.78
0.0644	271.169	5.2743	979.69
0.0644	275.228	5.5413	979.50
0.0644	277.197	5.7735	979.40
0.0644	279.077	6.1612	979.29
0.0644	281.138	6.6778	979.17
0.0644	283.174	7.2734	979.05
0.0644	285.090	7.9014	978.93
0.0644	287.166	8.6424	978.79
0.0644	289.215	9.4758	978.66
0.0644	291.118	10.2779	978.53
0.0644	293.130	11.1857	978.39
0.0644	295.150	12.1621	978.25
0.0644	297.210	13.1799	978.11
0.0644	299.188	14.1836	977.97
0.0644	301.105	15.1416	977.84
0.0955	260.150	3.7590	968.65
0.0955	261.148	3.7371	968.61
0.0955	262.122	3.7398	968.57
0.0955	263.162	3.7665	968.52
0.0955	264.110	3.8137	968.48
0.0955	265.150	3.8897	968.43
0.0955	269.175	4.4240	968.23
0.0955	271.180	4.8142	968.12
0.0955	275.150	5.8620	967.89
0.0955	277.210	6.4870	967.76
0.0955	279.120	7.1955	967.64
0.0955	281.079	7.9830	967.51
0.0955	282.800	8.7329	967.39
0.0955	287.059	10.858	967.09
0.0955	291.164	13.2028	966.79
0.0955	293.123	14.4209	966.65
0.0999	260.134	3.1443	971.40
0.0999	261.151	3.1468	971.36
0.0999	262.154	3.1739	971.31
0.0999	263.132	3.2211	971.27
0.0999	263.157	3.2251	971.27
0.0999	264.143	3.2979	971.22
0.0999	265.146	3.3965	971.17
0.0999	267.153	3.6547	971.07
0.0999	269.150	4.0017	970.97
0.0999	271.156	4.4377	970.85
0.0999	273.134	4.9520	970.74
0.0999	276.155	5.8935	970.55

Table I. (*Continued*)

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.0999	279.116	6.9953	970.36
0.0999	282.163	8.3092	970.16
0.0999	288.135	11.389	969.74
0.0999	288.142	11.389	969.74
0.0999	291.131	13.1716	969.52
0.0999	294.151	15.1254	969.30
0.1086	259.151	1.3751	964.04
0.1086	260.150	1.4171	963.99
0.1086	261.145	1.4836	963.95
0.1086	262.147	1.5720	963.90
0.1086	263.130	1.6765	963.85
0.1086	263.132	1.6866	963.85
0.1086	264.152	1.8241	963.80
0.1086	265.155	1.9817	963.75
0.1086	267.149	2.3556	963.64
0.1086	269.143	2.8126	963.53
0.1086	271.142	3.3495	963.41
0.1086	273.148	3.9350	963.29
0.1086	275.147	4.6331	963.16
0.1086	277.145	5.4094	963.03
0.1086	280.142	6.7187	962.82
0.1086	283.141	8.1933	962.61
0.1086	283.150	8.1984	962.61
0.1086	286.142	9.8684	962.40
0.1386	289.151	11.6395	962.18
0.1386	253.180	0.4835	956.40
0.1386	254.140	0.6193	956.35
0.1386	257.061	1.1591	956.19
0.1386	259.146	1.6466	956.07
0.1386	261.021	2.1461	955.96
0.1386	265.135	3.4694	955.71
0.1386	267.090	4.2045	955.58
0.1386	269.204	5.0716	955.44
0.1386	275.080	7.8927	955.03
0.1386	277.078	8.9832	954.88
0.1386	279.109	10.1573	954.73
0.1386	281.112	11.383	954.58
0.1386	283.134	12.6859	954.43
0.1436	285.173	14.0622	954.28
0.1436	267.152	0.2980	952.40
0.1436	268.149	0.7233	952.33
0.1436	269.151	1.1411	952.26
0.1436	270.151	1.6090	952.18
0.1436	271.150	2.0915	952.11

Table I. (*Continued*)

Mole fraction of Ammonia	Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
0.1436	273.151	3.1044	951.96
0.1436	275.150	4.1785	951.81
0.1436	277.151	5.2890	951.66
0.1436	279.149	6.4757	951.51
0.1436	282.150	8.4098	951.28
0.1436	285.148	10.4641	951.05
0.1436	285.15	10.4663	951.05
0.1436	288.151	12.6277	950.81
0.1436	273.151	3.1044	951.96
0.1436	275.150	4.1785	951.81
0.1436	277.151	5.2890	951.66
0.1436	279.149	6.4757	951.51
0.1436	282.150	8.4098	951.28
0.1436	285.148	10.4641	951.05
0.1436	285.15	10.4663	951.05
0.1436	288.151	12.6277	950.81

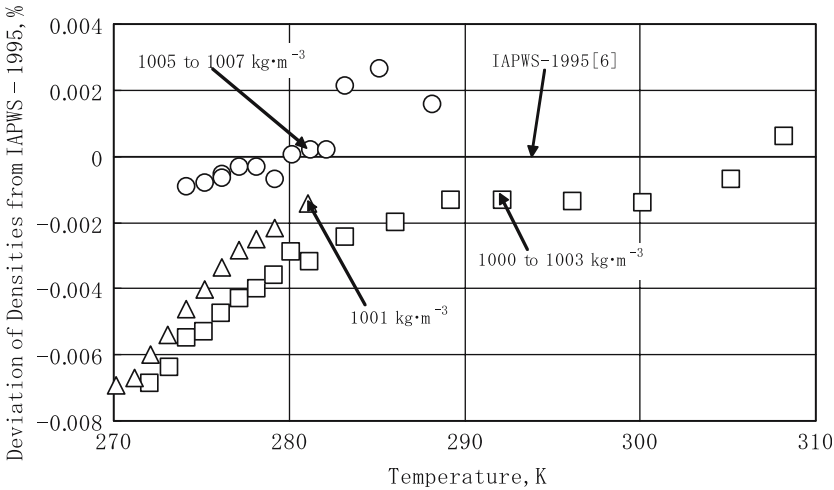

Fig. 1. Deviations of the measured densities for ordinary water substance from IAPWS-1995 Formulation [6].

of state by Tillner-Roth and Friend [1] gives pressures low in comparison with the present data.

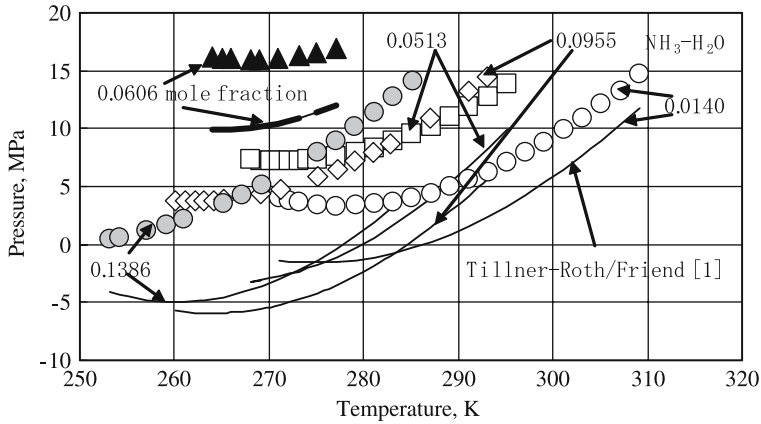

Fig. 2. Comparisons of the measured *pVTx* property data for aqueous solution of ammonia with the equation of state correlated by Tillner-Roth and Friend [1], solid lines.

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