

Vapor-Liquid Equilibria in the System $\text{NH}_3 + \text{H}_2\text{O} + \text{LiBr}$.

1. Measurements at $T = 303\text{--}423\text{ K}$ and $p = 0.1\text{--}1.5\text{ MPa}$

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A static method described in a previous paper has been used to obtain vapor-liquid equilibrium data for the system ammonia (NH_3) + water (H_2O) + lithium bromide (LiBr) at four temperatures, 303.15, 333.15, 373.15, and 423.15 K, and pressures up to 1.5 MPa. The salt concentration in the liquid phase was chosen in the range 5–60 mass % LiBr in pure water.

Introduction

Mixtures of ammonia, water, and lithium bromide provide a working fluid for absorption heat pumps and heat transformers as they are used today, for example, for air-conditioning purposes. Solutions with high salt concentrations have been considered as favorable working fluids for absorption machines like heat pumps, refrigerators, and heat transformers (1–4). For this reason vapor-liquid equilibrium (VLE) measurements in considerable ranges of pressure, temperature, and concentration have been undertaken (2, 5–6). The question of crystallization, which might occur in the liquid phase and cause serious problems during operation, has been considered by Peters et al. (7). Information about the density and viscosity of ammonia + water + lithium bromide solutions are given by Keller et al. (8). The intention of our work is to obtain systematic information on the VLE in the temperature range of 303–423 K and at pressures up to 1.5 MPa.

Experimental Section

Apparatus. The VLE measurements were made with the static method. The equilibrium cell, fabricated of chromium-nickel steel, has a volume of 452 cm³. The still is submerged in the oil bath of the thermostat. More details of the method and the apparatus used have been described by Zimmermann and Keller (5, 9). The schematic flow diagram is given in Figure 1.

Chemicals. Water was distilled twice and was mixed with lithium bromide of 99.4% purity (Riedel-de Haën AG). Ammonia and helium were supplied by Messer-Griesheim with a specified minimum purity of 99.999%.

Experimental Procedures. Initially, an aqueous lithium bromide solution of known composition was placed into the cell. Then ammonia was added. The liquid phase was stirred at 210 rpm till the pressure p and the temperature T were constant to $\pm 0.05\text{ K}$ and $\pm 5\text{ mbar}$, i.e., till equilibrium was reached. The liquid samples were withdrawn through a capillary and mixed with a given amount of bidistilled water in an aspirator bottle to allow the determination of the mass fractions of the components by using ion sensitive electrodes for Br^- and NH_4^+ . Some details of the procedure are given in the section below.

The sample of the vapor phase was diluted with helium and recirculated before it was injected directly into the gas chromatograph by an admission valve.

Temperature and Pressure Measurement. The pressure was measured with a pressure transducer (Sensotec,

Burster Präzisionsmesstechnik, type 8267 "TJE") with an accuracy of $\pm 0.02\text{ bar}$. The temperature was measured with a resistance thermometer (Heraeus, W-EOK) with a dispersion of $\pm 0.15\text{ K}$.

Composition Determination. The composition of the vapor phase ($\text{NH}_3 + \text{H}_2\text{O}$) was determined by a gas chromatograph (Perkin-Elmer, model 8410) augmented by a helium cycle. The chromatograph's column was filled with anteparon on chromosorb 104. Lithium bromide in the vapor phase was not investigated, because it was assumed that in the temperature and pressure ranges considered LiBr is only present in amounts which are not detectable by standard methods. In principle this can be checked by cooling the vapor phase and comparing p , T , x , and y data with those of the (well known) binary mixture $\text{NH}_3 + \text{H}_2\text{O}$ (6, 10, 11)! Because of corrosion problems in the gas circuit, probably caused by transfer of small droplets containing water and salt during intermittent cleaning processes, the vapor phase could be analyzed precisely only at $T = 373$ and 423 K .

The composition of the liquid phase was determined by ion sensitive electrodes. Ammonia could be directly measured by a gas sensitive electrode (Orion, EA 940, electrode 95-12), while the concentration of lithium bromide could only be obtained by titration (Orion 960, Autochemistry System). For the titration a solid-state electrode (silver-silver sulfide electrode) was used combined with a double-junction reference electrode. The titrant is a 0.1 M silver nitrate solution. The chemical reaction of titration is



The accuracies of concentrations determined by these methods are 1 mass % for ammonia and 0.3 mass % for lithium bromide. The concentrations of lithium bromide determined by weighing the sample and by titration were identical within the bounds of experimental errors.

Results

The results of the measurements are presented in Tables 1–32 and Figures 2–6. The data in each table are indicated by an average temperature and an initial salt concentration. Each data set includes the measured values of temperature and pressure and the mole fractions of ammonia and lithium bromide in the liquid phase. Tables 24–31 give the mole fraction of ammonia in the gas phase at 373.15 and 423.15 K. At 303.15 and 333.15 K the composition of the gas phase could be analyzed for a selected set of data only (Tables 1, 2, and 32).

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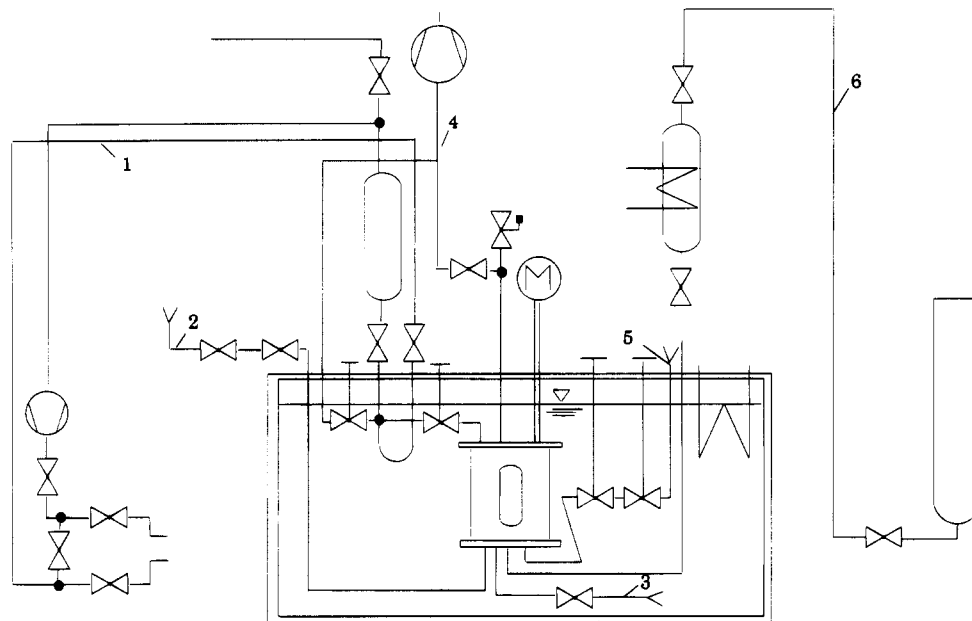


Figure 1. Schematic flow diagram of the apparatus (April 1994): (1) helium gas circuit; (2) H₂O + LiBr supply; (3) discharge of the mixture; (4) vacuum pump; (5) liquid sampling tube; (6) NH₃ supply.

Table 1. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.16 K, Initial Salt Concentrations 5 mass %

<i>T</i> /K	<i>p</i> /kPa	<i>x</i> _{NH₃}	<i>x</i> _{LiBr}	<i>y</i> _{NH₃}
333.15	100	0.0722	0.0075	0.7427
333.15	200	0.1929	0.0093	0.9409
333.17	300	0.3049	0.0093	0.9628
333.15	500	0.3472	0.0106	0.9861
333.17	700	0.4212	0.0098	0.9964
333.17	900	0.4615	0.0094	
333.15	1106	0.5746	0.0101	
333.15	1300	0.5913	0.0099	
333.31	1312	0.6983	0.0119	
333.07	1499	0.5954	0.0042	

Table 2. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.17 K, Initial Salt Concentration 10 mass %

<i>T</i> /K	<i>p</i> /kPa	<i>x</i> _{NH₃}	<i>x</i> _{LiBr}	<i>y</i> _{NH₃}
333.17	105	0.1601	0.0182	0.8615
333.20	201	0.2391	0.0170	0.9426
333.15	302	0.3320	0.0157	0.9806
333.12	700	0.3219	0.0109	
333.17	1106	0.5852	0.0105	
333.23	1303	0.6764	0.0110	

Table 3. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.15 K, Initial Salt Concentration 15 mass %

<i>T</i> /K	<i>p</i> /kPa	<i>x</i> _{NH₃}	<i>x</i> _{LiBr}
333.15	100	0.1185	0.0313
333.17	200	0.1877	0.0376
333.17	300	0.2131	0.0277
333.15	615	0.3366	0.0312
333.15	935	0.4218	0.0456
333.15	1164	0.4306	0.0289
333.14	1500	0.6016	0.0314

Figure 2 shows isobars (0.1–1.0 MPa) in a triangular phase diagram for the liquid phase at 303.15 K. The vapor pressure curves were correlated only by empirical lines. Following the isobar 0.4 MPa in Figure 2, the mass fraction of ammonia in the liquid phase slightly decreases with increasing salt concentration. At high salt concentrations, which means mass fractions of 50% lithium bromide in water, the mass fraction of ammonia in the liquid phase is higher than in the binary ammonia + water system at the

Table 4. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.15 K, Initial Salt Concentration 20 mass %

<i>T</i> /K	<i>p</i> /kPa	<i>x</i> _{NH₃}	<i>x</i> _{LiBr}
333.17	100	0.1494	0.0373
333.15	200	0.1827	0.0351
333.17	300	0.2572	0.0328
333.15	503	0.3051	0.0329
333.15	700	0.3500	0.0262
333.14	905	0.3843	0.0254
333.18	1103	0.4183	0.0217
333.15	1499	0.5337	0.0181

Table 5. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.16 K, Initial Salt Concentration 25 mass %

<i>T</i> /K	<i>p</i> /kPa	<i>x</i> _{NH₃}	<i>x</i> _{LiBr}
333.15	100	0.1393	0.0523
333.01	203	0.1827	0.0450
333.17	311	0.3017	0.0475
333.17	501	0.3689	0.0371
333.20	702	0.5004	0.0370
333.12	943	0.4884	0.0355
333.09	1191	0.5754	0.0278
333.09	1311	0.6086	0.0286
333.12	1501	0.6233	0.2390

Table 6. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.12 K, Initial Salt Concentration 30 mass %

<i>T</i> /K	<i>p</i> /kPa	<i>x</i> _{NH₃}	<i>x</i> _{LiBr}
333.07	102	0.1947	0.0692
333.20	217	0.2366	0.0623
333.15	310	0.2652	0.0604
333.12	506	0.3208	0.0547
333.09	704	0.3766	0.0546
333.02	917	0.4957	0.0468
333.12	1101	0.4990	0.0439
333.15	1500	0.5687	0.0367

same temperature. This effect increases with increasing vapor pressure. Considering a line from the lithium bromide apex of the triangular diagram to a concentration at the triangle's base line referring to the binary ammonia + water, the ratio of the mass fractions of ammonia to water is a constant. Following such a line, the vapor pressure increases at the beginning of the addition of

Table 7. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.19 K, Initial Salt Concentration 35 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
333.20	102	0.1933	0.0835
333.20	199	0.2199	0.0819
333.20	301	0.2674	0.0777
333.20	500	0.3254	0.0695
333.23	703	0.3551	0.0635
333.17	924	0.4664	0.0591
333.17	1101	0.4982	0.0515
333.17	1506	0.4855	0.0431

Table 8. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.18 K, Initial Salt Concentration 40 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
333.17	107	0.1772	0.0936
333.15	200	0.2156	0.0921
333.20	301	0.2829	0.0871
333.20	500	0.3772	0.0750
333.17	906	0.5149	0.0614
333.17	1132	0.5462	0.0561
333.17	1301	0.5852	0.0485
333.20	1502	0.6224	0.0488

Table 9. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.15 K, Initial Salt Concentration 47 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
333.17	103	0.2457	0.1134
333.17	334	0.2979	0.1027
333.17	500	0.4308	0.0953
333.17	704	0.4376	0.0913
333.17	899	0.4704	0.0762
333.17	1119	0.5323	0.0743
333.17	1305	0.5767	0.0690
333.04	1513	0.6814	0.0591

Table 10. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.18 K, Initial Salt Concentration 54 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
333.20	103	0.3035	0.1394
333.17	200	0.3541	0.1356
333.34	300	0.3765	0.1338
333.12	504	0.4199	0.1242
333.20	703	0.5243	0.1049
333.17	900	0.5896	0.0999
333.12	1100	0.6289	0.0901
333.12	1299	0.7771	0.0831
333.20	1520	0.8164	0.0700

Table 11. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 333.08 K, Initial Salt Concentration 60 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
332.54	108	0.4192	0.1731
333.12	205	0.4445	0.1600
333.15	301	0.5203	0.1547
333.23	541	0.5216	0.1426
333.17	914	0.6383	0.1208
333.17	1300	0.6838	0.1170
333.20	1498	0.8292	0.1016

lithium bromide to the liquid phase. At higher concentrations of lithium bromide in the liquid phase the vapor pressure first tends to the value of the binary ammonia + water and then decreases further on. The same phase behavior could be observed at 333.15 K, shown in Figure 3. What does this mean as far as the affection of the molecules in the liquid phase is concerned? The measured data points in the triangular diagrams indicate that, at high mass fractions of lithium bromide, not only the ions

Table 12. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.30 K, Initial Salt Concentration 5 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.21	103	0.2509	0.0076
303.73	197	0.3588	0.0077
303.13	306	0.4237	0.0077
303.21	504	0.5412	0.0075
303.21	710	0.6352	0.0054

Table 13. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.05 K, Initial Salt Concentration 10 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
302.93	105	0.2835	0.0150
303.11	202	0.3984	0.0156
303.16	304	0.4734	0.0125
302.98	556	0.5622	0.0115

Table 14. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.16 K, Initial Salt Concentration 15 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.24	99	0.2800	0.0222
303.16	232	0.3746	0.0216
303.13	413	0.5096	0.0186
303.21	496	0.5382	0.0172
303.23	594	0.5667	0.0161
303.16	702	0.6065	0.0128
303.06	923	0.7471	0.0080
303.11	1002	0.7875	0.0050

Table 15. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.16 K, Initial Salt Concentration 20 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.18	102	0.3324	0.0315
303.13	210	0.4216	0.0305
303.16	300	0.4577	0.0291
303.16	441	0.5193	0.0278
303.16	508	0.5381	0.0261
303.15	654	0.6335	0.0203

Table 16. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.18 K, Initial Salt Concentration 25 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.06	202	0.4121	0.0438
303.16	397	0.4832	0.0346
303.21	606	0.5541	0.0255
303.23	857	0.6506	0.0197
303.23	1001	0.6750	0.0098

Table 17. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.23 K, Initial Salt Concentration 30 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.16	104	0.3431	0.0473
303.16	195	0.4168	0.0490
303.61	462	0.5265	0.0408
303.23	100	0.3402	0.0594
303.21	306	0.4594	0.0435
303.18	549	0.5207	0.0379
303.21	692	0.5788	0.0326
303.13	798	0.6608	0.0246
303.15	924	0.7597	0.0195

Li^+ and Br^- seemingly attract water molecules but ammonia does also.

In Figure 4 the vapor pressure above an ammonia + water + lithium bromide solution with an initial salt concentration of 26.6 mass % is plotted against the mole fractions of ammonia in the liquid and the gas phase at 373.15 K. As can be seen, both the vapor pressure and

Table 18. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.16 K, Initial Salt Concentration 35 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.23	200	0.3762	0.0614
303.13	397	0.4817	0.0522
303.13	612	0.5834	0.0434
303.18	912	0.7399	0.0193
303.13	1038	0.8365	0.0136

Table 19. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.18 K, Initial Salt Concentration 40 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.16	99	0.3202	0.0658
303.11	410	0.4909	0.0603
303.21	598	0.6000	0.0499
303.11	104	0.3107	0.0775
303.23	302	0.4336	0.0658
303.23	498	0.5460	0.0551

Table 20. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.19 K, Initial Salt Concentration 45 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.23	103	0.2918	0.0914
303.23	199	0.3585	0.0838
303.18	406	0.4666	0.0688
303.18	591	0.5549	0.0541
303.16	813	0.6721	0.0473
303.13	983	0.7721	0.0218

Table 21. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.12 K, Initial Salt Concentration 50 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.13	101	0.3354	0.1024
303.11	200	0.4322	0.0984
303.08	301	0.4485	0.0911
303.08	407	0.4815	0.0859
303.13	498	0.5163	0.0777
303.08	592	0.5755	0.0696
303.11	761	0.6442	0.0606
303.18	906	0.7178	0.0475
303.15	995	0.8301	0.0299
303.16	1084	0.8874	0.0205

Table 22. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.15 K, Initial Salt Concentration 55 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.13	101	0.4216	0.1275
303.06	217	0.4903	0.1163
303.11	602	0.6183	0.0840
303.18	824	0.6836	0.0695
303.08	991	0.8659	0.0200
303.21	95	0.3665	0.1427
303.13	96	0.3382	0.1273
303.18	501	0.5199	0.1034
303.21	709	0.6358	0.0819
303.16	920	0.7666	0.0545
303.21	1038	0.8383	0.0356

the mole fraction of ammonia in the gas phase increase at constant ammonia concentration in the liquid phase referring to the binary system $\text{NH}_3 + \text{H}_2\text{O}$. Figure 5 shows the phase envelope for a ternary solution with 54.6 mass % salt concentration referring to $\text{H}_2\text{O} + \text{LiBr}$ at 423.15 K. The vapor pressure curve is shifted to lower vapor pressures indicated by the values measured by Pawlikowsky et al. (11) for the ammonia + water system. The diagrams show that, by adding LiBr to a mixture of $\text{NH}_3 + \text{H}_2\text{O}$, the vapor pressure curve systematically is shifted to the low water content regime. However, the shift decreases con-

Table 23. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 303.18 K, Initial Salt Concentration 60 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}
303.23	99	0.3917	0.1370
303.23	309	0.5502	0.1227
303.13	494	0.5677	0.1171
303.13	707	0.6701	0.0956
303.21	893	0.8651	0.0732
303.18	892	0.8383	0.0715
303.18	998	0.8857	0.0471
303.16	999	0.8704	0.0466

Table 24. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 374.53 K, Initial Salt Concentration 5 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
373.2	61	0.0002	0.0138	
374.9	282	0.1142	0.0101	0.2424
374.8	476	0.1653	0.0093	0.6509
374.7	674	0.2790	0.0089	0.7284
374.7	884	0.0002	0.0138	0.8001
374.7	1106	0.1142	0.0101	0.8608
374.7	1253	0.3531	0.0077	0.9263
374.6	1459	0.3866	0.0071	0.9688

Table 25. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 374.74 K, Initial Salt Concentration 14 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
374.7	62	0.0007	0.0327	0.0029
374.7	274	0.0663	0.0316	0.3419
374.7	490	0.1313	0.0251	0.6644
374.7	888	0.1824	0.0295	0.9479
374.9	1450	0.3197	0.0244	

Table 26. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 374.99 K, Initial Salt Concentration 20 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
375.0	111	0.0136	0.0501	0.7637
375.0	260	0.0790	0.0477	0.9167
375.1	347	0.1011	0.0468	0.9088
374.9	444	0.1350	0.0403	0.9496
374.9	583	0.1745	0.0384	0.9462
375.1	747	0.2343	0.0391	0.9569
375.1	940	0.2376	0.0374	0.9586
375.2	1117	0.2617	0.0384	0.9647
374.7	1290	0.2788	0.0345	0.9748
374.9	1469	0.3190	0.0302	

Table 27. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 374.51 K, Initial Salt Concentration 26.6 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
374.5	115	0.0249	0.0699	0.4721
374.7	198	0.0611	0.0650	0.6647
374.5	407	0.0739	0.0627	0.8386
374.5	603	0.1012	0.0645	0.8782
374.5	721	0.1992	0.0594	0.9202
374.5	842	0.1488	0.0613	0.9298
374.5	1014	0.1921	0.0524	0.9307
374.5	1298	0.2569	0.0502	0.9583
374.4	1507	0.2820	0.0494	0.9744

siderably with increasing total pressure. Besides, it seems to be negligible below 20 mass % LiBr referred to a mixture of $\text{H}_2\text{O} + \text{LiBr}$.

Computer calculations to correlate the phase behavior of ammonia + water + lithium bromide solutions are under way and will be presented in another paper in this journal.

Industrial Aspects

The main disadvantages of the well-known ammonia + water system as the working fluid in heat pumps and heat

Table 28. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 425.90 K, Initial Salt Concentration 28 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
420.5	262	0.0050	0.0746	0.0076
426.3	410	0.0134	0.0863	0.2700
426.6	520	0.0382	0.0938	
426.7	715	0.0792	0.1093	0.6431
426.8	951	0.1211	0.1013	0.7244
426.7	1163	0.1355	0.0985	0.8398
426.7	1360	0.1475	0.0927	0.8369
426.9	1548	0.1690	0.0877	0.8682

Table 29. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 430.35 K, Initial Salt Concentration 50 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
430.4	329	0.0503	0.1709	0.7456
430.5	472	0.0989	0.1614	0.7530
430.4	717	0.1272	0.1610	0.8889
430.3	878	0.1652	0.1515	0.9422
430.3	1071	0.1645	0.1454	0.7334
430.2	1249	0.1748	0.1440	0.8305
430.1	1480	0.1809	0.1367	0.9159

Table 30. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 427.14 K, Initial Salt Concentration 50 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
426.7	381	0.1010	0.1696	
427.3	493	0.1461	0.1694	0.6985
427.3	602	0.1589	0.1779	0.5754
427.2	805	0.1519	0.1702	0.7837
427.1	942	0.1162	0.0945	0.7934
427.1	1145	0.1688	0.1546	0.8551
427.3	1323	0.1851	0.1596	0.8957

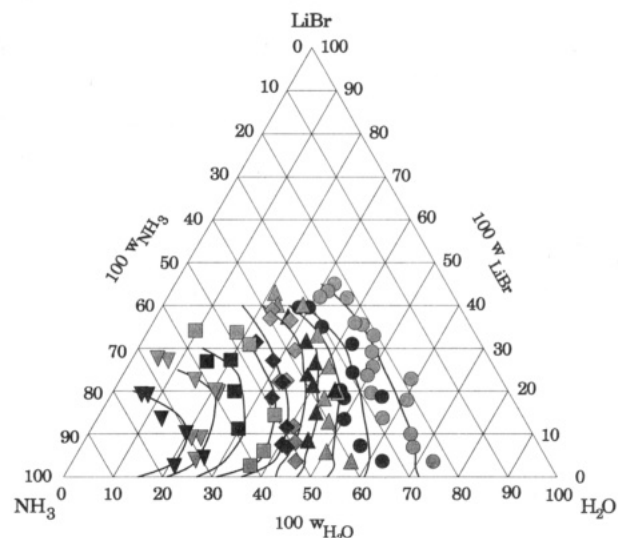
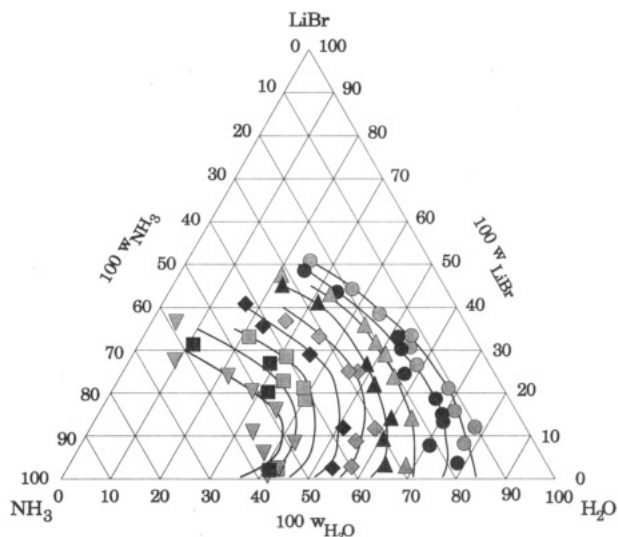
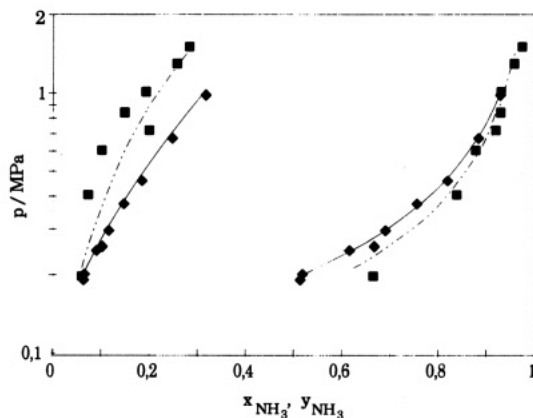
Table 31. Ammonia + Water + Lithium Bromide Equilibrium Data, Average Temperature 426.86 K, Initial Salt Concentration 54.6 mass %

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
422.8	95	0.0002	0.1997	0.0021
427.1	216	0.0041	0.1818	0.5739
427.0	391	0.0247	0.1291	0.7585
428.9	601	0.1166	0.1561	0.7954
427.2	749	0.1637	0.1435	0.8705
427.1	922	0.1753	0.1402	0.8897
427.1	1083	0.1940	0.1353	0.9107
427.1	1230	0.2044	0.1338	0.9164
427.2	1372	0.2500	0.1354	0.9317
427.1	1585	0.2434	0.1234	0.9222

Table 32. Ammonia + Water + Lithium Bromide Equilibrium Data, Particular Data Points

T/K	p/kPa	x_{NH_3}	x_{LiBr}	y_{NH_3}
343.2	1618	0.5161	0.0306	0.9924
323.3	997	0.5028	0.0319	0.9813
333.2	1279	0.5337	0.0317	0.9757
299.7	451	0.4589	0.0330	0.9688
301.2	658	0.5405	0.0267	0.9815
304.4	337	0.4125	0.0943	0.9985
306.8	74	0.1729	0.0543	0.8782
306.9	576	0.4717	0.0371	0.9697
309.4	153	0.2384	0.0481	0.9631
310.6	269	0.3395	0.0406	0.9460

transformers are the water content in the vapor phase, leading to an expensive dephlegmator, and high vapor pressures at elevated temperatures. Mixtures of water and lithium bromide with high salt concentrations are well-suited absorption fluids for ammonia vapor. Hence, at a given temperature, in the vapor phase the partial pressures of both water and ammonia are reduced compared to the respective pressures in the $\text{NH}_3 + \text{H}_2\text{O}$ system. Therefore,

**Figure 2.** Ternary diagram of the system ammonia + water + lithium bromide presenting liquid states at 303.15 K: (shaded \circ) 0.1 MPa; (\bullet) 0.2 MPa; (shaded \triangle) 0.3 MPa; (\blacktriangle) 0.4 MPa; (shaded \diamond) 0.5 MPa; (\blacklozenge) 0.6 MPa; (shaded \square) 0.7 MPa; (\blacksquare) 0.8 MPa; (shaded ∇) 0.9 MPa; (\blacktriangledown) 1.0 MPa.**Figure 3.** Ternary diagram of the system ammonia + water + lithium bromide presenting liquid states at 333.15 K: (shaded \circ) 0.1 MPa; (\bullet) 0.2 MPa; (shaded \triangle) 0.3 MPa; (\blacktriangle) 0.5 MPa; (shaded \diamond) 0.7 MPa; (\blacklozenge) 0.9 MPa; (shaded \square) 1.1 MPa; (\blacksquare) 1.3 MPa; (shaded ∇) 1.5 MPa.**Figure 4.** Phase diagram of the system ammonia + water + lithium bromide presenting vapor-liquid equilibria at 373.15 K: initial salt concentration, 26.6 mass %; (\blacklozenge) $\text{NH}_3 + \text{H}_2\text{O}$, data points from Müller (10); (\blacksquare) $\text{NH}_3 + \text{H}_2\text{O} + \text{LiBr}$.

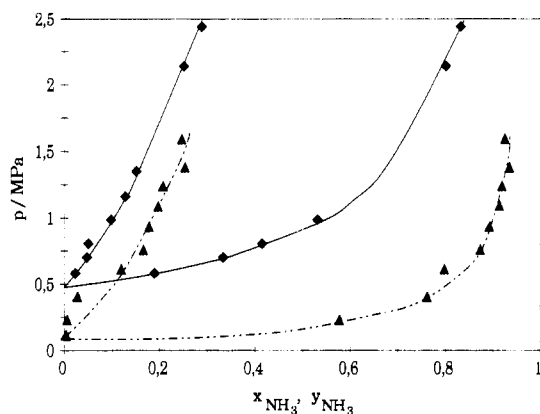


Figure 5. Phase diagram of the system ammonia + water + lithium bromide presenting vapor-liquid equilibria at 423.15 K: initial salt concentration, 54.6 mass %; (◆) $\text{NH}_3 + \text{H}_2\text{O}$, data points from Pawlikowski et al. (11); (▲) $\text{NH}_3 + \text{H}_2\text{O} + \text{LiBr}$.

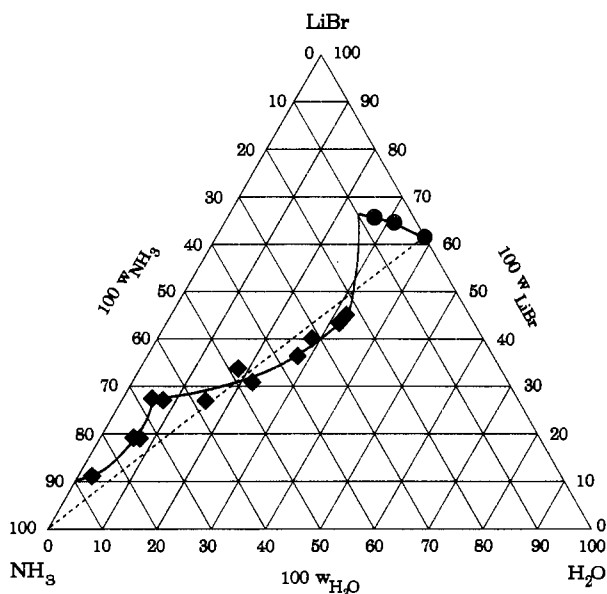


Figure 6. Ternary diagram of the system ammonia + water + lithium bromide presenting states of crystallization at 303.15 K (7): (shaded ○) solubility data; (◆) triple points.

the vapor above ternary solutions of $\text{NH}_3 + \text{H}_2\text{O} + \text{LiBr}$ at high pressures still contains small amounts of water. The dephlegmator cannot be avoided for this system.

Ternary solutions with an initial concentration of 60 mass % LiBr have been considered as favorable working fluids for sorption processes by Radermacher (2) and Radermacher and McLinden (12). Figure 6 shows the

crystallization line in the ammonia + water + lithium bromide system at 303.15 K. As can be seen from the phase diagram in Figure 6, a straight line connecting the LiBr + H_2O side at 60 mass % and the state of pure ammonia (NH_3) will intersect the three-phase (SVLE-(solid-liquid-vapor equilibrium)) region. On part of this line the steady states of an absorption heat pump must even out. More details of the crystallization states in the system ammonia + water + lithium bromide are given by Peters et al. (7).

As far as industrial aspects are concerned, mixtures of H_2O and LiBr with high salt concentrations do not seem to be favorable solvents for ammonia. Also, one has to take into account that adding lithium bromide to ammonia + water solutions will cause serious corrosion problems and an increase in the solvent's viscosity (8). This is a major result of our work.

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