

Solid-Liquid Equilibria in the Systems NH₃-H₂O-LiBr and H₂O-LiBr at $p = 1$ atm in the Range from -35 to 80°C ¹

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Solid-liquid equilibria at ambient pressure and solid-liquid-vapor equilibria at $T = 303.15$ K have been measured in the system ammonia-water-lithium bromide for various initial concentrations of lithium bromide. Liquid phases have been analyzed using ion selective electrodes. A ternary phase diagram of the system at $T = 303.15$ K is provided showing a triple line and several regions in which solid phases of different kind occur. This will restrict considerably the use of these systems as working fluids in absorption machinery.

KEY WORDS: absorption processes; ammonia; crystallization temperatures; solid-liquid equilibria; lithium bromide, solubility curve; triple line; vapor-liquid equilibria.

1. INTRODUCTION

The system ammonia-water-lithium bromide with high salt concentrations has been considered as a favorable working fluid for absorption machines such as heat pumps, refrigerators, and heat transformers [1-4]. For this reason vapor-liquid equilibria (VLE) measurements in a considerable range of pressure, temperature, and concentration have been undertaken [5, 6]. However, the question of crystallization, which might occur in the liquid phase and cause serious problems during operation, has not been considered in this work. This is the main goal of this paper: to provide information about solid-liquid-vapor equilibria (SLE) in the system

¹ Paper dedicated to Professor Joseph Kestin.

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$\text{NH}_3\text{-H}_2\text{O-LiBr}$, in order to decide the concentration range within which this system actually could be used in absorption machinery. The industrially oriented experiments performed in our laboratory were: (i) freezing experiments of ammonia water solutions augmented with different amounts of lithium bromide at ambient pressure and (ii) triple state experiments at $T = 303.15\text{ K}$ in the range 0.1–1.1 MPa.

In Section 2 the experimental procedures are described. In Section 3 we give results, thermodynamic data of SLE states at ambient pressure and SLVE states at 303.15 K. Some photographs taken at the onset and during crystallization within and above a liquid phase also will be given and discussed to a certain extent. Unfortunately, the solid phases could not be isolated and analyzed for composition and crystalline properties, this being postponed for future investigations. As a result it can be stated that the system $\text{NH}_3\text{-H}_2\text{O-LiBr}$ exhibits, at 303.15 K and high concentrations of lithium bromide, i.e., about 60 wt%, a considerable region within which a solid phase, consisting presumably of $(\text{LiBr} \cdot \text{NH}_3 \cdot \text{H}_2\text{O})$, will occur. This certainly should be taken into account in designing and operating industrial absorption cycles.

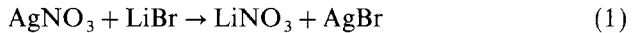
2. EXPERIMENTS

2.1. Solubility Curve

Encountering crystallization phenomena in the system $\text{NH}_3\text{-H}_2\text{O-LiBr}$, we were restricted to consider mixtures of lithium bromide and ammonia-water solutions containing about 25 wt% NH_3 , at ambient pressure and a temperature range from 239 to 362 K. Lithium bromide of 99.4 wt% purity (Riedel-de Haën AG) was given in a lab flask of 100-ml contents, then weighed using an analytical balance (Mettler, AE 260). Then the ammonia-water solution was added, leading to a considerable increase in temperature and loss of certain amounts of both ammonia and water vapor. Weighing the sample again, the concentration of lithium bromide in the mixture can be determined. To check reliability of this datum and also to measure the concentration of ammonia, we decided to use ion selective electrodes.

Ammonia can be measured directly by a gas-sensitive electrode (Orion, EA 940, electrode 95-12), while the concentration of lithium bromide can be obtained only by titration (Orion 960, Autochemistry System). For the titration a solid-state electrode (silver-silver sulfide electrode) is used combined with a double-junction reference electrode.

The titrant is a 0.1M silver nitrate solution. The chemical reaction of titration is



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

After preparing a liquid mixture of LiBr, H_2O , NH_3 , the flask was suspended in a cryogenic thermostat (Schott, CT-2, CT 1150, isopropyl alcohol). The thermostat was cooled by a refrigerator using methanol as working fluid (Lauda, Ultra-Kryomate KW90SW). The thermostat was equipped with a slit-like window, allowing observation of the onset of crystallization in the flask for temperatures above 268 K. Below this temperature, the window was always covered with ice. Therefore, to observe crystallization, the flask had to be removed from the bath.

Solutions of LiBr, NH_3 , H_2O which were already saturated at room temperature, i.e., contained a solid phase, were heated in a thermostat and slowly cooled down until the onset of crystallization could be observed. The temperature was measured during experiments by a glass thermometer (AL-LHU) and a temperature probe (Impac, Tastootherm UP1300). In the region of onset of crystallization it could be observed within 0.5 K.

Experiments of the kind described above naturally are confined to a small region of ammonia concentration, i.e., $w_{\text{NH}_3} < 9$ wt%. This is due mainly to the low content of ammonia in a saturated ammonia-water solution at ambient pressure and temperature.

2.2. Triple Line

Using a static still, VLE in the ternary system ammonia-water-lithium bromide have been measured in the range 303–423 K and 0.1–1.5 MPa. Some details of the method and the apparatus used have been described by Zimmermann and Keller [5, 6].

Initially, a well-known aqueous lithium bromide solution was filled into the cell. Then ammonia with a purity of 99.999% (Messer Griesheim) was added. The liquid phase was stirred at 210 rpm till the pressure p and the temperature T assumed constant values, i.e., equilibrium was reached. The pressure was measured with a pressure transducer (Sensotec, Burster Präzisionsmeßtechnik, Type 8267 "TJE") with an accuracy of ± 0.02 bar; the temperature was measured with a resistance thermometer (Heraeus, W-EOK) with a dispersion of ± 0.15 K. The composition of the liquid

phase was determined with ion-sensitive electrodes (ORION) as described in Section 2.1. The composition of the vapor phase ($\text{NH}_3\text{-H}_2\text{O}$) was determined with a gas chromatograph augmented by a helium cycle operating at 160°C . These measurements were limited to high concentrations of lithium bromide by the triple line. For practical reasons the triple line could be examined only at 303.15 K . Adding ammonia to a binary liquid mixture of $\text{H}_2\text{O/LiBr}$ at this temperature sometimes caused the occurrence of dustlike crystals in the liquid phase, which dissolved again later. At high concentrations of lithium bromide, the crystals settled out. After hours a state of solid-liquid-vapor equilibrium (SLVE) was attained and a sample of the liquid phase could be withdrawn. The composition of this sample was determined by ion-sensitive electrodes and checked for thermodynamic consistency using VLE data, knowing the isobars (VLE) to be limited by the triple line (SLVE).

3. RESULTS

3.1. Solubility Curve

In this section, we present experimental values of the solubility of lithium bromide in water and water-ammonia solutions, i.e., solid-liquid equilibria of the systems $\text{H}_2\text{O-LiBr}$ and $\text{NH}_3\text{-H}_2\text{O-LiBr}$ at ambient pressure. The data also are sketched in a temperature-concentration diagram (T, w_{LiBr}). The onset of crystallization at three different concentrations and respective temperatures is depicted in a set of photos.

In order to check the reliability of the method to determine the temperature at the onset of crystallization, described in Section 2, experiments

Table I. Crystallization Points of Aqueous Lithium Bromide Solutions at 1 atm.

Temperature (K)	Concentration of Lithium bromide (%)
309.15	64.01
301.15	61.64
288.15	59.30
269.65	56.65
260.15	53.98
251.15	52.20
242.15	50.49

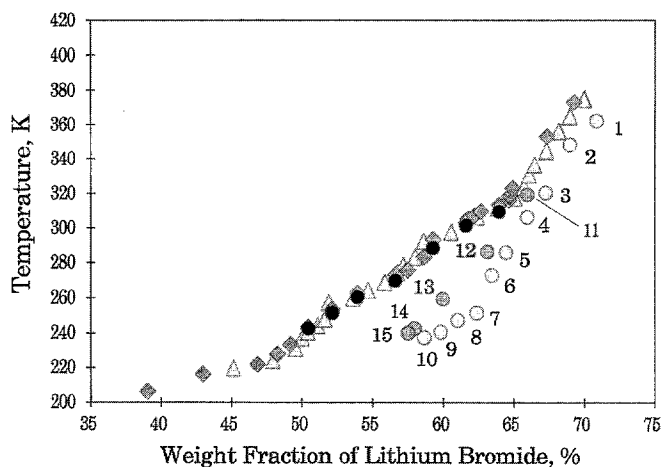


Fig. 1. Solubility curve of aqueous lithium bromide and aqueous ammonia-lithium bromide solutions at 1 atm. This work ($\text{NH}_3\text{-H}_2\text{O-LiBr}$) (\odot, \bullet); this work ($\text{H}_2\text{O-LiBr}$) (\bullet); Kessis ($\text{H}_2\text{O-LiBr}$) [7] (\triangle); Boryta ($\text{H}_2\text{O-LiBr}$) [8] (\diamond).

Table II. Crystallization Points of Aqueous Ammonia Lithium Bromide Solutions at 1 atm.

Temperature (K)	Concentration (%) of		Sample No.
	Lithium bromide	Ammonia	
362.15	70.90	4.58	1
348.15	69.03	3.45	2
320.15	67.30	7.65	3
306.15	66.00	6.96	4
285.65	64.50	8.58	5
272.65	63.50	8.08	6
251.15	62.40	8.75	7
247.15	61.04	8.28	8
240.15	59.84	8.32	9
237.15	58.69	8.01	10
319.15	66.03	3.88	11
286.15	63.16	4.46	12
259.15	60.00	3.36	13
242.15	58.00	3.44	14
239.65	57.54	2.96	15

with water–lithium bromide solutions were performed. Results are given in Table I. The experimental data show good agreement with those measured by Kessis [7] and Boryta [8], as can be seen in Fig. 1.

Table II presents crystallization temperatures in the system ammonia–water–lithium bromide. The concentrations of ammonia and lithium bromide are given as percentage weight. In the fourth column the number of each sample is noted, referring also to the labels in Fig. 1.

In Fig. 1 crystallization temperatures of the system H_2O –LiBr at ambient pressure measured by Kessis [7], by Boryta [8], and in this work are plotted as a function of the concentration of lithium bromide in the range $38 < w_{\text{LiBr}} < 70$ wt %. In addition, crystallization temperatures of the system NH_3 – H_2O –LiBr corresponding to two different sets of measurements are presented. In the first set, experiments 1–10, ammonia–water solutions with $w_{\text{NH}_3} = 25$ wt % were used, whereas in the second set, Nos. 11–15, experiments were performed using initially ammonia–water solutions with $w_{\text{NH}_3} = 12.5$ wt %. Hence the concentrations of ammonia and lithium bromide in any two samples taken from different sets having (nearly) the same crystallization temperature differ considerably. This can be seen by comparing samples 3 and 11, 5 and 12, etc. As a rule, by adding ammonia to water–lithium bromide solutions, the onset of crystallization at ambient pressure and a given temperature is always shifted to higher concentrations of lithium bromide. Similarly, at a given concentration of lithium bromide the crystallization temperature of a ternary solution of NH_3 – H_2O –LiBr is always lower than that of the corresponding H_2O –LiBr solution.

Figures 2 and 3 include photos of crystals which occurred at two different temperatures in experiment 3 (cf. Table II). At 43°C primary crystallites appeared somewhat below the surface of the liquid phase (Fig. 2), showing a tendency for sedimentation at the bottom of the flask. The crystals seem to be nearly identical, exhibiting a triclinic, pyramid-like structure. Figure 3, taken at $T = 33^\circ\text{C}$, shows the flask with crystals having gathered at the bottom.

In experiment 4, a solution containing initially the same concentration of lithium bromide as solution 3 (cf. Table II), was cooled down starting at 40°C . The onset of crystallization could be observed at 33°C . At 20°C the bulk of the liquid phase was crystallized, a photo of which state is shown in Fig. 4. In the lower part, crystals of the type shown in Fig. 2 still can be recognized. Above them, branch-like fractal clusters of small crystals sticking to the walls of the flask can be seen. They are shown in more detail in Fig. 5.

Finally, Fig. 6 depicts small crystals which occurred at the walls of the flask above the liquid meniscus of solution 8 (cf. Table II) at 20°C , i.e.,



Fig. 2. The first primary crystallites appearing in the liquid phase of sample 3 at 43°C . Concentrations: 67.3 wt% LiBr, 7.65 wt% NH_3 , and 25.05 wt% H_2O .



Fig. 3. Starlike crystals growing in the liquid phase of sample 3 at 33°C . Initial concentrations: 67.3 wt% LiBr, 7.65 wt% NH_3 , and 25.05 wt% H_2O .

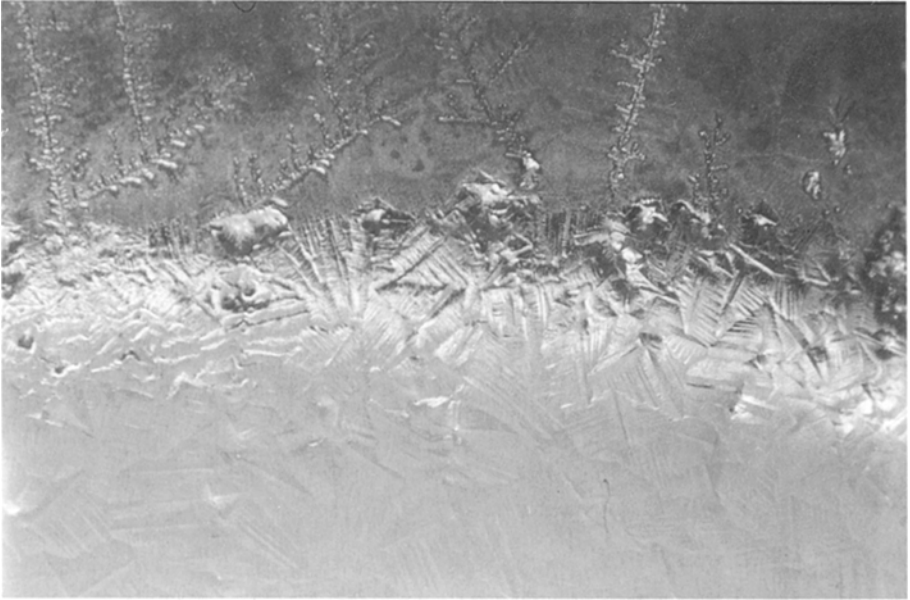


Fig. 4. The liquid phase of sample 4 is completely solidified at 20°C. Concentrations: 67.3 wt% LiBr, 7.65 wt% NH₃, and 25.05 wt% H₂O.

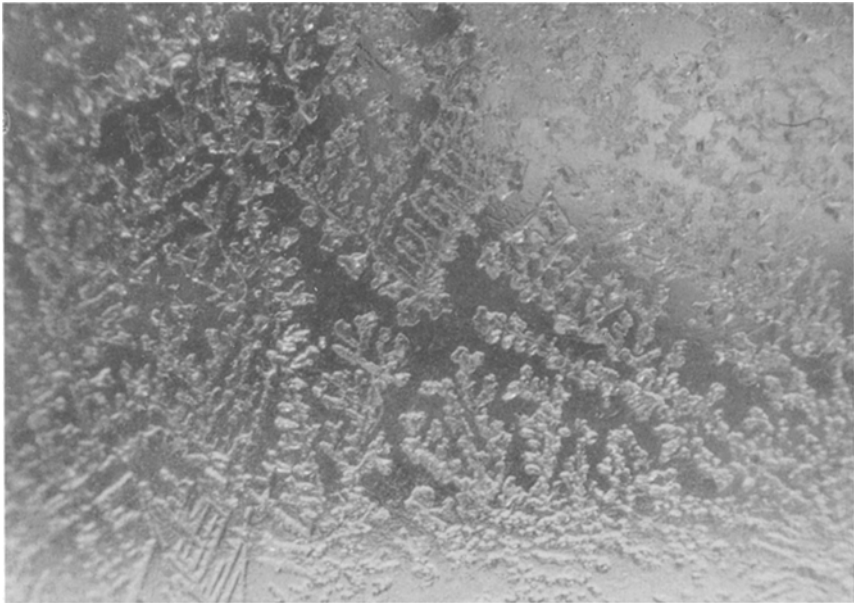


Fig. 5. Fractal structure of crystals at the wall of the flask above the bulk of sample 4 at 20°C. Initial concentrations of the liquid phase: 67.3 wt% LiBr, 7.65 wt% NH₃, and 25.05 wt% H₂O.

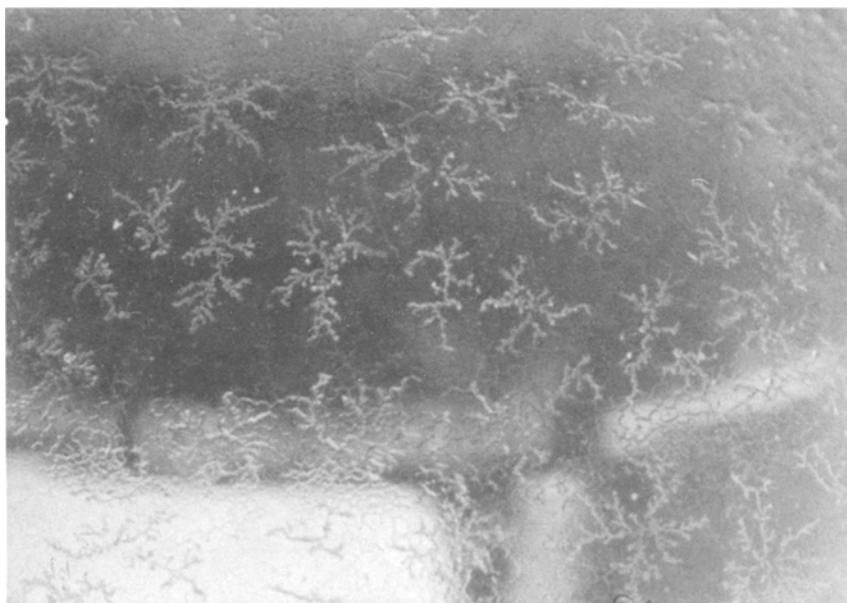


Fig. 6. Fractal structure of crystals at the wall of the flask above the liquid phase of sample 6 at 20°C. Concentration of the liquid phase: 63.5 wt % LiBr, 8.08 wt % NH_3 , and 28.42 wt % H_2O at 20°C.

46 K above the onset of freezing of the liquid. These crystals also show fractal structures. By shaking the flask, they easily could be dissolved in the liquid phase. However, they could be observed again after several hours.

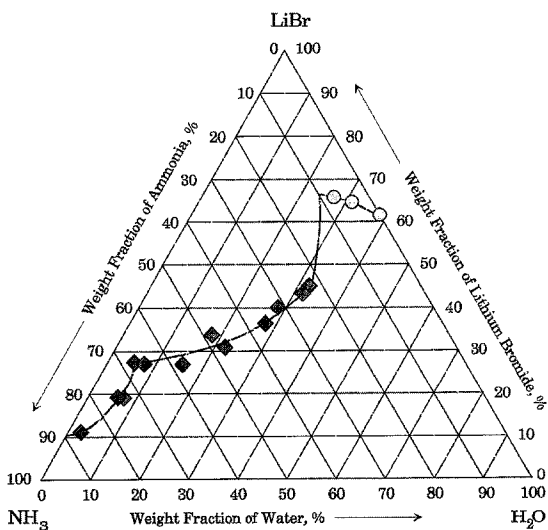
Unfortunately, we were not able to isolate and analyze any of the crystals observed visually, this task being left to future investigations.

3.2. Triple Line

In this section we are going to report on the triple line of the system ammonia–water–lithium bromide at 30°C. Since experiments turned out to be cumbersome and elaborate, only 12 measurements of SLVE could be performed. As expected these states turned out to be limiting states of a nearly continuous set of VLE, being realized in a static still at constant temperature and contents of water and lithium bromide but increasing amounts of ammonia. In Table III the experimental values of SVLE are given, i.e., the pressure p in MPa and the weight fractions of ammonia and lithium bromide in wt %, at 303.15 K. The weight fraction of water can be calculated from these data as the supplement to 100 wt %. Figure 7 illustrates data points in the respective ternary diagram.

Table III. Triple Points of Ammonia–Water–Lithium Bromide Solutions at 303.15 K.

Pressure (MPa)	Concentration (%) of	
	Lithium bromide	Ammonia
0.095	45.09	22.72
0.099	43.35	24.89
0.299	40.15	31.50
0.501	36.47	35.96
0.707	33.76	48.23
0.709	30.89	47.02
0.821	26.98	57.59
0.892	27.07	65.31
0.893	27.58	67.15
0.998	19.23	74.63
0.999	19.08	73.38
1.084	11.19	86.25

**Fig. 7.** Ternary diagram of the system ammonia–water–lithium bromide presenting states of crystallization at 303.15 K. Solubility data (⊙); triple points (◆).

The triple line can be divided into three different sections. The first section starts near the state of pure ammonia and includes four data points ranging between 10 and 28 wt% LiBr, 86 and 65 wt% NH_3 , and 1.1 and 0.9 MPa. The solid phase (γ) probably consists of $\text{LiBr}(\text{NH}_3)_2$ crystals, [9, 10]. The second part of the triple line including seven data points ranges from 28 to 45 wt% LiBr and 65 to 22 wt% NH_3 at pressures from 0.9 to 0.1 MPa. The solid phase (β) is assumed to consist of $\text{LiBr}(\text{NH}_3 \cdot \text{H}_2\text{O})$. Since measurements were limited to pressures above 0.1 MPa, the three data points depicted in the third part of the triple line do not represent true SVLE states but were calculated from solubility data of LiBr in $\text{NH}_3\text{-H}_2\text{O}$ solutions at low concentrations of NH_3 , around 30°C , as included in Table II. These data seem to be a fair approximation of the SLVE data at 30°C in the range 0–0.1 MPa since normally the concentration of phases in SLE states at a given temperature does not depend strongly on the (low) pressure in the system. The solid phase (α) in this interpolated section of the triple line consists of $\text{LiBr}(\text{H}_2\text{O})_2$ crystals, [7]. The gap of miscibility seemingly occurring between the triple state measured at 45.09 wt% LiBr, 22.72 wt% NH_3 , 0.1 MPa and the SLE state of $\text{LiBr-H}_2\text{O}$ at the same pressure, indicated in the triangular diagram, seems to be actually realized. This is a consequence inevitably from our experiments with $\text{LiBr}(\text{H}_2\text{O})_2$ crystals at very low pressures, $p \rightarrow 0$, which almost suddenly were liquified when only small amounts of ammonia were added.

4. DISCUSSION AND CONCLUSIONS

Due to the triple states of the system $\text{NH}_3\text{-H}_2\text{O-LiBr}$ observed at 303.15 K, a triangular phase diagram has been developed (Fig. 8). It includes three solid phases, namely, (α) $\text{LiBr} \cdot 2\text{H}_2\text{O}$, (β) $\text{LiBr} \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$, and (γ) $\text{LiBr} \cdot 2\text{NH}_3$. They have been chosen according to the literature [7, 10].

The key point to understanding the diagram is the state where the β phase, i.e., lithium bromide-monoammonium-monohydrate only exists (Z_β). It terminates five lines separating various two- and three-phase regions as indicated in Fig. 8. Approaching Z_β from the two-phase region ($L + \beta$), one will find equilibrium states Z consisting of the solid phase β , a liquid phase (Z_1), the concentration of which is given by the intersection of the conode with the triple line below, thus assuming the mass of the vapor phase related to Z considered to be negligible. The ($L + \beta$) region is neighbored by several small regions describing states consisting of three condensed, i.e., solid or liquid, phases and a vapor phase.

As far as industrial aspects are concerned, mixtures of H_2O and LiBr

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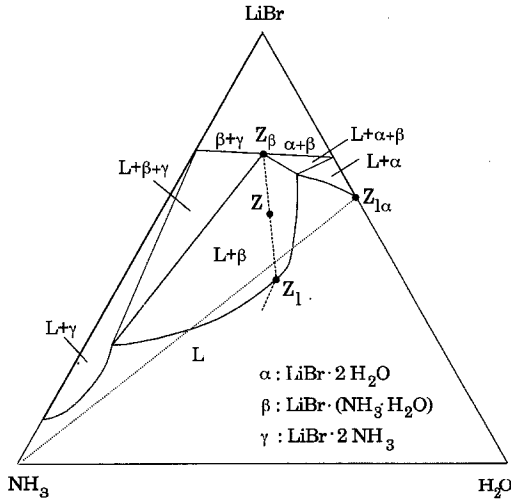


Fig. 8. Triangular phase diagram of the system ammonia-water-lithium bromide at 303.15 K.

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with high salt concentrations do not seem to be favorable solvents for ammonia. This is a major result of this work. Indeed, as can be seen from the phase diagram (Fig. 8), a straight line connecting the S, L state on the LiBr, H_2O line, $Z_{1\alpha}$, with the state of pure ammonia will intersect the region $(L + \beta)$, i.e., inevitably the solid phase β will occur. Also, one has to take into account that adding LiBr to $\text{NH}_3\text{-H}_2\text{O}$ solutions will cause serious corrosion problems and an increase in the solvent's viscosity [11].

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