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Measurements of Vapor–Liquid Equilibria in the Systems NH_3–H_2O–NaOH and NH_3–H_2O–KOH at Temperatures of 303 and 318 K and Pressures 0.1 MPa $< p <$ 1.3 MPa

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A static method has been used to obtain vapor–liquid equilibrium data for the systems ammonia (NH_3)–water (H_2O)–potassium hydroxide (KOH) and ammonia–water–sodium hydroxide (NaOH) at temperatures of 303 and 318 K and pressures from 0.1 to 1.3 MPa. The salt concentration in the liquid phase was chosen in the range from 2 to 60 mass% salt in water. In both systems NH_3–H_2O–NaOH and NH_3–H_2O–KOH, solid–liquid–vapor equilibria were observed. In the NH_3–H_2O–KOH system, liquid–liquid–vapor equilibrium was observed at 318 K and 1.1 MPa but at yet unknown concentrations of the liquid phases.

KEY WORDS: absorption working fluids; ammonia–water–potassium hydroxide; ammonia–water–sodium hydroxide; static equilibrium cell; vapor–liquid equilibria.

1. INTRODUCTION

The binary system ammonia–water is a well-known working fluid for absorption cooling systems. One of the disadvantages of this working fluid is the considerable amount of water in the vapor phase. To overcome this difficulty, it has been proposed to add a second component to the solvent water [1], for example, lithium nitrate [2], or lithium bromide [3, 4]. Unfortunately, it turned out that the mixture containing lithium bromide is not a suitable working fluid for absorption cooling systems because of

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crystallization [5]. Searching for alternative additives, several authors suggested adding sodium hydroxide or potassium hydroxide to the ammonia–water system [6]. Hence, it became desirable to obtain vapor–liquid equilibria (VLE) data for these systems at technically important temperatures for comparison with those of the ammonia–water system.

VLE were measured in this study for the ternary electrolyte systems ammonia–water–sodium hydroxide (NH_3–H_2O–NaOH) and ammonia–water–potassium hydroxide (NH_3–H_2O–KOH) at the temperatures 303 and 318 K. In both systems the pressure was limited to $p < 1.3$ MPa due to the occurrence of solid phases. Measurements were made using the static method described in Ref. 1. The vapor phase was analyzed using a gas chromatograph with helium as a carrier gas. Details have been given in Refs. 1 and 7. It turned out that the ammonia concentrations of the gaseous phase were always higher than or at least equal to 99.5 mass% and the water concentrations lower than 0.5 mass%. No evidence of the presence of salts in the vapor phase was found.

The liquid phase was analyzed for its ammonia concentration by chemical titration [1]. Its salt concentration was determined from a mass balance [1].

The measured VLE data are presented in tables and ternary diagrams. The effect of salt on the vapor pressure of the classic ammonia–water system is discussed to some extent.

2. EXPERIMENTAL

Measurements of VLE in the systems ammonia–water–sodium hydroxide (NH_3–H_2O–NaOH) and ammonia–water–potassium hydroxide (NH_3–H_2O–KOH) were performed using the static method described previously [1]. A schematic of the experimental setup is given in Fig. 1. Its main part is a vessel, a so-called static equilibrium cell to hold both the liquid and the vapor phases of a fluid system at a given temperature and pressure. The vessel is made of stainless steel and equipped with windows (sapphire glass) for optical inspection. The vessel is connected to several tubes used for evacuation and filling purposes. The installation uses a liquid recirculation loop for mixing the phases and for taking a sample for analysis. The vessel, most of the tubing, and the liquid recirculation pump are located within a thermostatted bath using oil (Baysilon M20, BAYER AG, Germany) as the heat transfer fluid.

The temperature in the cell is measured with a platinum resistance thermometer (Pt 100) with an uncertainty of ±0.15 K. The pressure in the cell is measured with a high-precision pressure transducer, allowing uncertainties of ±2 kPa at pressures up to 2 MPa. Isothermal measurements

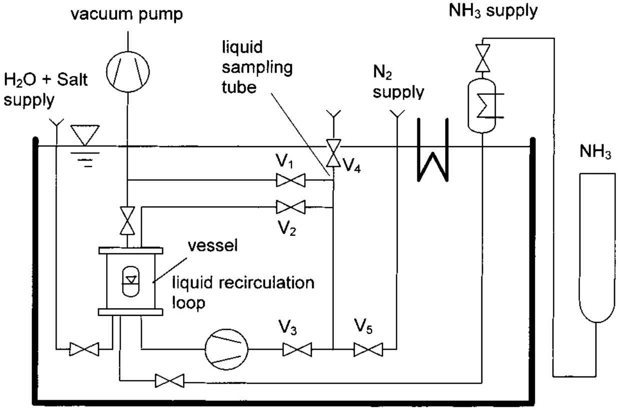

Fig. 1. Schematic of the static VLE apparatus.

were performed as follows. The evacuated equilibrium cell was filled with a solution of water–salt made of double-distilled, degassed water and sodium hydroxide pellets (Riedel de Haen; purity, >99 mass% NaOH) or potassium hydroxide pellets (Riedel de Haen; purity, >85 mass% KOH, <1 mass% K_2CO_3; residuals, water). In view of the low-purity standard of the KOH pellets, the exact potassium hydroxide concentration in the solution was determined by titration with hydrochloride. The pressure in the equilibrium cell was adjusted by adding gaseous ammonia (Messer Griesheim, purity 99.999 mass%). When the temperature and pressure in the cell were constant for at least 1 h, thermodynamic equilibrium was assumed. Then a sample of the liquid phase was taken as follows. The liquid phase was pumped around the liquid loop with valves V_2 and V_3 open and valves V_1, V_4, and V_5 closed. Then valves V_2 and V_3 were closed and V_4 and V_5 were opened, and the trapped sample between V_2 and V_3 was transferred to a steel vessel using pressurized nitrogen. The sample vessel was prepared by filling it with double-distilled water which was pressurized with nitrogen at a pressure well above the pressure in the equilibrium cell.

The sample of liquid phase dissolved in water was analyzed as follows. Sulfuric acid was added, and by back-titration with sodium hydroxide, the number of moles of ammonia and sodium/potassium hydroxide was determined. From this and from the known salt concentration of the solution, which was filled in the equilibrium cell at the beginning, the concentrations of ammonia and sodium/potassium hydroxide were calculated.

The gas phase was analyzed only at the lowest pressure (0.1 MPa) and the highest pressure (<1.3 MPa) realized in the cell. At both temperatures,

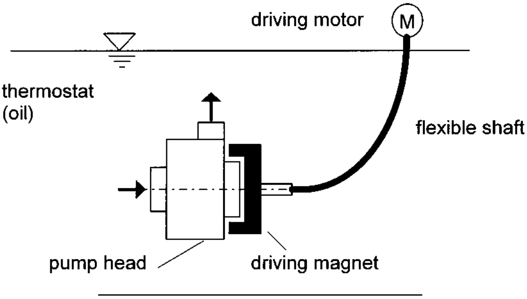

Fig. 2. Schematic of the liquid recirculation pump.

303 and 318 K (as well as 333 K), and all pressure levels analyzed, it turned out that the ammonia concentration in the vapor phase was always higher than or at least 99.5 wt%, whereas the water concentration was lower than or at most 0.5 wt%. Salt was not found in the vapor samples according to the temperatures and pressures measured in recondensation experiments leading to LVE states of nearly pure ammonia. In view of this, the pressure in the cell was increased by simply adding pure ammonia. Equilibration was enhanced by using the circulation loop and a magnetic stirrer. Phase equilibria, i.e., constant values of pressure and temperature, were always reached after less then 10 min. Despite this fact, samples for analysis were taken only after maintaining phase equilibria for 1 h! The pump in the liquid circulation loop was Type C-101 (Ismatec, Wertheim, Germany). It can handle corrosive fluids at temperatures of $273\ \mathrm{K} < T < 423\ \mathrm{K}$ and pressures of $0 < p < 1.4$ MPa. The pump is located at the lowest level in the thermostated bath (see Fig. 2). The head of the pump is driven by a magnetic clutch, which is connected through a flexible shaft to the electric prime mover placed outside the thermostat.

3. RESULTS

The results of the measurements are presented in Tables I to IV and Figs. 3 to 10. In Figs. 3 to 6 the ammonia concentration in the liquid phase is plotted versus the vapor pressure of the system. The ratio of water and salt concentrations and the temperature in the system are constant! The various symbols correspond to liquid solutions whose initial salt concentration, referring to the ammonia free initial state, is indicated in the figures.

The solid line represents the ammonia–water system calculated with the association model from Peters and Keller [1]. A comparison of Figs. 3–6 results in two simple statements.

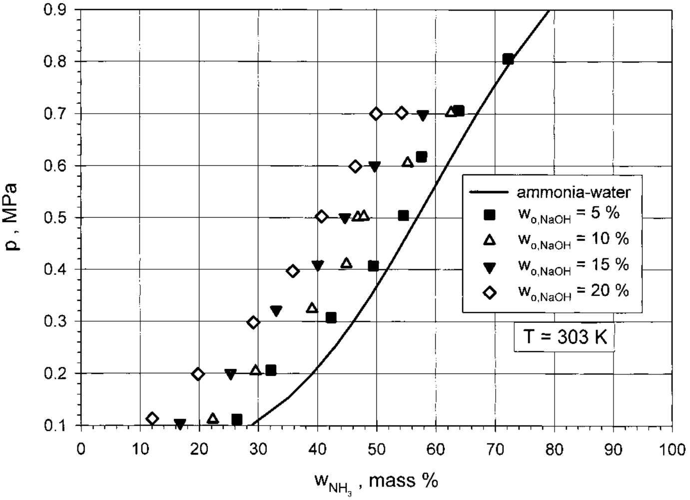

Fig. 3. Pressure–composition diagram of the ammonia–water–sodium hydroxide system with data for the liquid state at 303 K. The solid line represents results for the ammonia–water system calculated using the model of Keller and Peters [1].

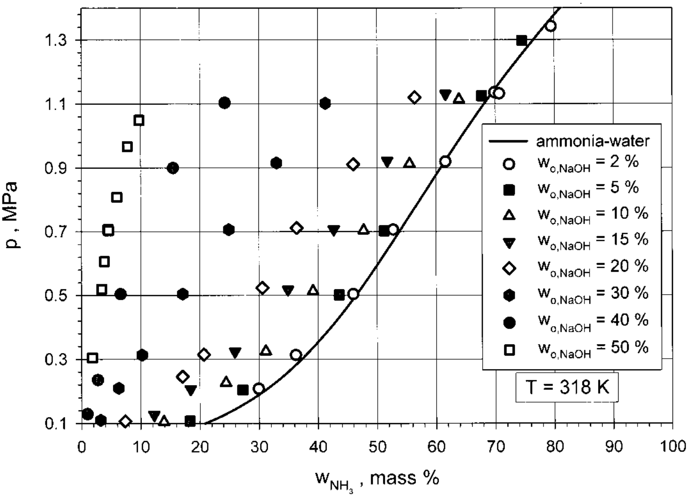

Fig. 4. Pressure–composition diagram of the ammonia–water–sodium hydroxide system with data for the liquid state at 318 K. The solid line represents results for the ammonia–water system calculated using the model of Keller and Peters [1].

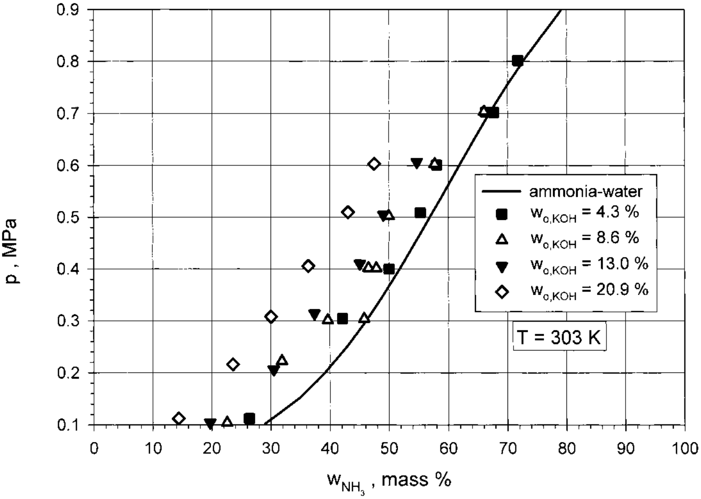

Fig. 5. Pressure–composition diagram of the ammonia–water–potassium hydroxide system with data for the liquid state at 303 K. The solid line represents results for the ammonia–water system calculated using the model of Keller and Peters [1].

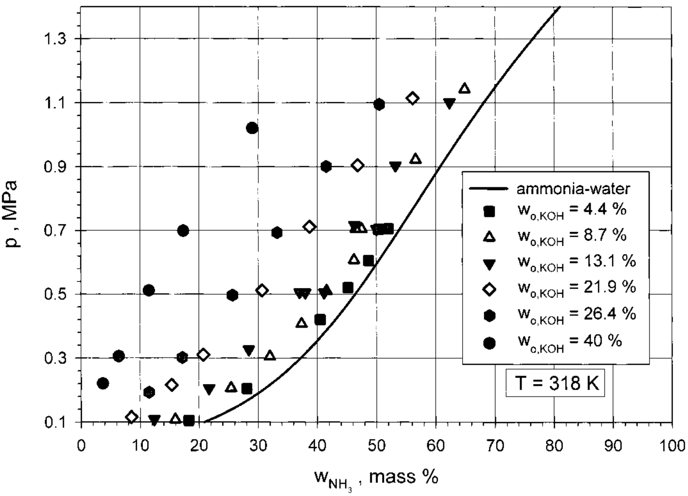

Fig. 6. Pressure–composition diagram of the ammonia–water–potassium hydroxide system with data for the liquid state at 318 K. The solid line represents results for the ammonia–water system calculated using the model of Keller and Peters [1].

Table I. VLE Data for NH_3–H_2O–NaOH at 303 K

p (MPa)	T (K)	w_{NH_3} (mass %)	w_{NaOH} (mass %)
0.1118	303.09	26.32	3.68
0.2064	303.21	32.12	3.39
0.3073	303.09	42.30	2.89
0.4072	303.10	49.48	2.53
0.5045	303.23	54.57	2.27
0.6182	303.22	57.60	2.12
0.7064	303.24	63.84	1.81
0.8058	303.21	72.18	1.39
0.1115	303.22	22.25	7.78
0.2040	303.22	29.54	7.05
0.3238	303.23	39.06	6.09
0.4108	303.21	44.90	5.51
0.5008	303.23	46.82	5.32
0.5021	303.23	47.84	5.22
0.6057	303.23	55.27	4.47
0.7021	303.24	62.55	3.75
0.1045	303.21	16.75	12.49
0.2004	303.21	25.27	11.21
0.3220	303.14	33.02	10.05
0.4095	303.22	40.05	8.99
0.5009	303.21	44.64	8.30
0.6011	303.23	49.66	7.55
0.6993	303.22	57.82	6.33
0.1129	303.13	12.06	17.59
0.1985	303.17	19.80	16.04
0.2978	303.18	29.18	14.16
0.3967	303.16	35.82	12.84
0.5026	303.19	40.71	11.86
0.5994	303.19	46.42	10.72
0.7001	303.20	49.91	10.02
0.7019	303.20	54.24	9.15

- The ammonia concentration in the liquid phase decreases on adding either sodium hydroxide or potassium hydroxide to the ammonia–water system.
- The ammonia concentration in the liquid phase decreases with an increase in temperature.

Figures 7–10 show Gibbs diagrams of the liquid phase of the systems NH_3–H_2O–NaOH and NH_3–H_2O–KOH at 303 and 318 K. The various symbols correspond to isobaric states as indicated in the figures. The

Table II. VLE Data for NH_3–H_2O–NaOH at 318 K

p (MPa)	T (K)	w_{NH_3} (mass%)	w_{NaOH} (mass%)
0.2084	318.19	29.92	1.40
0.3134	318.16	36.22	1.28
0.5038	318.05	45.93	1.08
0.7064	318.05	52.74	0.95
0.9199	318.27	61.59	0.77
1.1357	318.27	69.85	0.60
1.1323	318.22	70.66	0.59
1.3423	318.12	79.46	0.41
0.1075	318.12	18.32	4.08
0.2047	318.19	27.24	3.64
0.5011	318.16	43.57	2.82
0.7024	318.25	51.21	2.44
1.1252	318.23	67.72	1.61
1.2973	318.28	74.49	1.28
0.1051	318.19	13.90	8.61
0.2269	318.17	24.40	7.56
0.3253	318.18	31.11	6.89
0.5132	318.19	39.16	6.08
0.7042	318.22	47.70	5.23
0.9129	318.22	55.51	4.45
1.1134	318.21	63.89	3.61
0.1269	318.16	12.26	13.16
0.2070	318.08	18.42	12.24
0.3245	318.07	25.93	11.11
0.5182	318.05	34.89	9.77
0.7072	318.12	42.66	8.60
0.9223	318.13	51.73	7.24
1.1307	318.11	61.61	5.76
0.1066	318.15	7.34	18.53
0.2459	318.20	17.08	16.58
0.3149	318.16	20.70	15.86
0.5236	318.15	30.57	13.8.9
0.7115	318.10	36.41	12.72
0.9115	318.18	45.95	10.81
1.1203	318.18	56.38	8.72
0.1100	318.18	3.19	29.04
0.2099	318.16	6.23	28.13
0.3136	318.19	10.21	26.94
0.5047	318.16	17.11	24.87
0.7066	318.15	24.91	22.53
0.9160	318.13	32.95	20.12
1.1024	318.13	41.26	17.62
0.1294	318.17	0.99	39.60
0.2355	318.15	2.72	38.91
0.5041	318.18	6.58	37.37
0.9000	318.19	15.49	33.80
1.1039	318.22	24.25	30.30
0.3050	318.03	1.79	49.11
0.5194	318.08	3.40	48.30
0.6064	318.10	3.85	48.08
0.7072	318.11	4.47	47.77
0.7037	318.09	4.54	47.73
0.8083	318.09	5.95	47.03
0.9671	318.13	7.73	46.14
1.0497	318.18	9.73	45.14

Table III. VLE Data for NH_3–H_2O–KOH at 303 K

p (MPa)	T (K)	w_{NH_3} (mass %)	w_{KOH} (mass %)
0.1120	303.16	26.36	3.17
0.3042	303.20	42.08	2.50
0.4004	303.18	49.99	2.16
0.5090	303.23	55.26	1.93
0.6012	303.20	58.01	1.81
0.7023	303.19	67.66	1.39
0.7025	303.22	66.31	1.45
0.8016	303.21	71.73	1.22
0.1040	303.20	22.58	6.63
0.2225	303.19	31.85	5.83
0.3039	303.17	45.77	4.64
0.3011	303.20	39.64	5.17
0.4020	303.19	46.50	4.58
0.4017	303.21	47.83	4.47
0.5024	303.20	49.96	4.28
0.6030	303.19	57.69	3.62
0.7034	303.20	66.01	2.91
0.1040	303.19	19.69	10.45
0.2061	303.22	30.48	9.04
0.3142	303.18	37.37	8.15
0.4103	303.19	45.03	7.15
0.5052	303.19	49.03	6.63
0.6071	303.20	54.69	5.89
0.1122	303.21	14.40	17.86
0.2160	303.18	23.59	15.95
0.3078	303.20	30.04	14.60
0.4057	303.20	36.34	13.29
0.5098	303.20	43.06	11.88
0.6032	303.21	47.45	10.97

pressure was limited to a value of about 1.3 MPa by the appearance of solid phases.

The Gibbs diagrams of the ammonia–water–sodium hydroxide and ammonia–water–potassium hydroxide systems are very similar. The decrease in the ammonia concentration in the liquid is more pronounced on adding sodium hydroxide than on adding potassium hydroxide to the ammonia–water system.

To understand the decrease in the ammonia concentration in the liquid phase upon adding alkali hydroxides, one has to be aware of the fact that ammonia and water molecules in liquid solutions are strongly coupled. This is reflected in the heat of evaporation of ammonia/water solutions,

Table IV. VLE Data for NH_3–H_2O–KOH at 318 K

p (MPa)	T (K)	w_{NH_3} (mass %)	w_{KOH} (mass %)
0.1044	318.09	18.25	3.61
0.2047	318.12	28.07	3.18
0.4199	318.13	40.48	2.63
0.5204	318.16	45.18	2.42
0.6055	318.15	48.70	2.27
0.7033	318.17	50.34	2.19
0.7054	318.17	51.98	2.12
0.1078	318.16	15.93	7.32
0.2064	318.17	25.40	6.50
0.3047	318.19	31.99	5.92
0.4066	318.16	37.36	5.46
0.5100	318.18	41.56	5.09
0.6068	318.17	46.20	4.69
0.7046	318.15	47.48	4.57
0.7050	318,15	46.50	4.66
0.9226	318.16	56.59	3.78
1.1422	318.15	64.89	3.06
0.1084	318.14	12.36	11.53
0.2057	318.12	21.69	10.31
0.3270	318.13	28.39	9.42
0.5045	318.12	37.99	8.16
0.7050	318.18	50.00	6.58
0.5045	318.18	41.16	7.86
0.5060	318.08	37.03	8.09
0.7169	318.13	46.27	6.90
0.9042	318.16	53.20	6.01
1.1015	318.17	62.34	4.84
0.1154	318.32	8.53	19.99
0.2156	318.22	15.35	18.50
0.3102	318.15	20.70	17.33
0.5115	318.10	30.66	15.15
0.7112	318.16	38.72	13.39
0.9048	318.20	46.82	11.62
1.1139	318.16	56.10	9.59
0.0909	318.24	5.94	24.84
0.1927	318.18	11.50	23.37
0.3014	318.21	17.14	21.88
0.4963	318.09	25.66	19.63
0.6929	318.16	33.22	17.64
0.9009	318.10	41.52	15.44
1.0949	318.14	50.48	13.08
0.2206	318.12	3.69	38.05
0.3056	318.16	6.37	36.99
0.5114	318.19	11.47	34.98
0.6986	318.21	17.31	32.67
1.0210	318.23	28.99	28.06

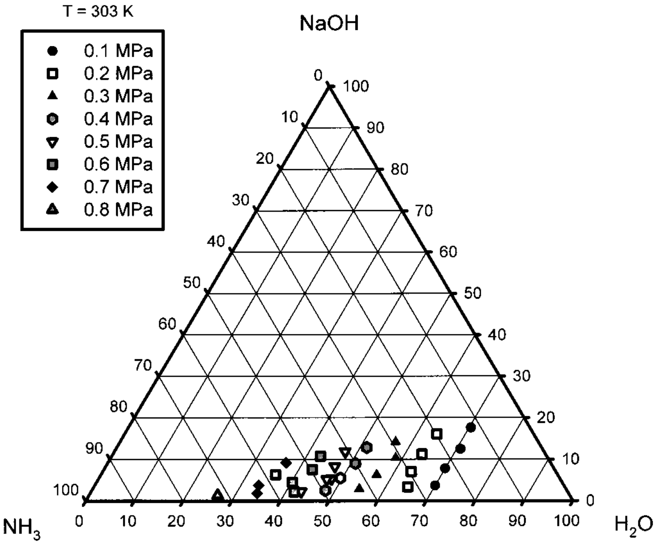

Fig. 7. Ternary diagram of the ammonia–water–sodium hydroxide system with isobaric data for the liquid state at 303 K. Concentrations in mass%.

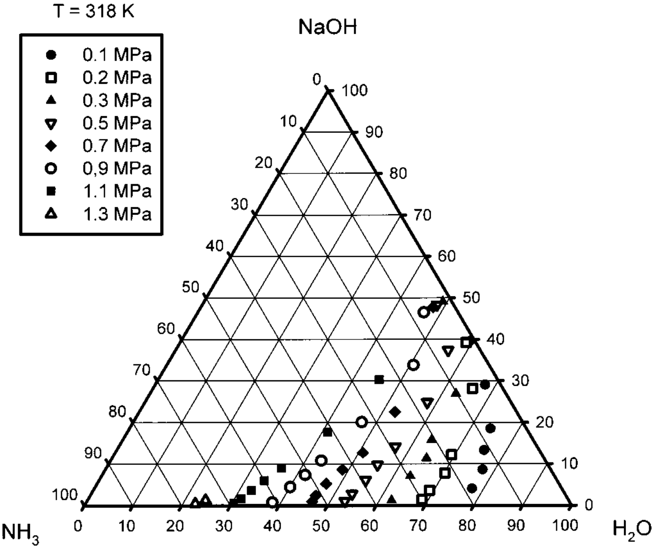

Fig. 8. Ternary diagram of the ammonia–water–sodium hydroxide system with isobaric data for the liquid state at 318 K. Concentrations in mass%.

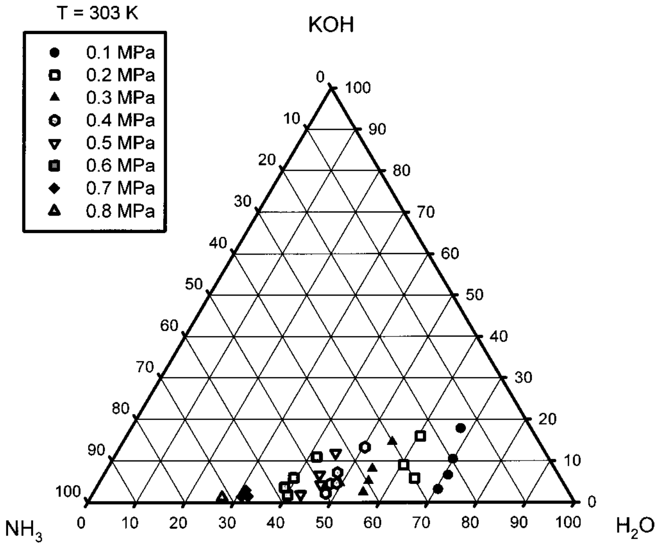

Fig. 9. Ternary diagram of the ammonia–water–potassium hydroxide system with isobaric data for the liquid state at 303 K. Concentrations in mass%.

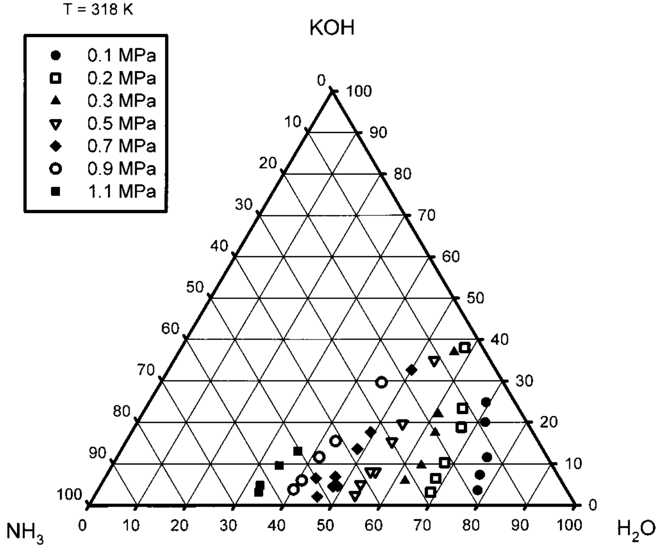

Fig. 10. Ternary diagram of the ammonia–water–potassium hydroxide system with isobaric data for the liquid state at 318 K. Concentrations in mass%.

which is approximately equal to that of pure water! Indeed, ammonia and water molecules in a liquid phase form $(NH_3 \cdot H_2O) = (NH_4^+ OH^-)$ clusters which can be considered new types of molecules in the solution [1, 3, 5, 8]. On adding alkalihydroxide (MOH; M = Na, K) these clusters are broken up! The "free" water molecules now available in the solution are used to become part of a shell around either of the ions of the alkalihydroxide or, especially at higher temperatures, the alkali hydroxide molecule itself [1]. The corresponding stochiometric formula of this solvation reaction in terms of molecules is

$$(NH_3 \cdot H_2O) + MOH^- \rightarrow NH_3\uparrow + (MOH \cdot H_2O)$$

In terms of ions it likewise can be written

$$(NH_4^+ \cdot OH^-) + M^+OH^- \rightarrow NH_3\uparrow + (M^+ \cdot H_2O \cdot OH^-)$$

The ammonia molecule produced, no longer finding "free" water which could be used to form a new cluster, will leave the liquid phase, thus increasing the partial pressure of ammonia in the vapor phase. This increase in the vapor pressure has been observed experimentally many times, sometimes, upon adding a large amount of alkalihydroxide pellets to ammonia–water solutions under environmental conditions (293 K, 1 bar), as ammonia explosions from the liquid phase combined with considerable heating effects. The substitution of ammonia by alkalihydroxide and its ions in ammonia–water–alkalihydroxide solutions is somewhat more pronounced for sodium than for potassium. This indicates that water molecules are more attracted by sodium hydroxide and its ions than by potassium hydroxide and its ions. This can be deduced from the data given in Tables I–IV by appropriate interpolation and comparison of corresponding VLE states. It also is supported by the fact that the dynamic viscosity of liquid sodium hydroxide–water–ammonia solutions is always higher by approximately 10 to 30% than the viscosity of potassium hydroxide–water–ammonia solutions at the same molecular concentrations, temperature, and pressure [1]. This again indicates that the Arrhenius water shells around sodium hydroxide and its ions are somewhat larger and more stable than the shells around potassium hydroxide [9].

Solid–liquid–vapor equilibria (SLVE) were observed in both ternary systems at the temperatures and pressures given in Table V. Figure 11 shows a photograph of SLVE in NH_3–H_2O–NaOH at 0.7 MPa. Unfortunately, the concentrations of the solid and liquid phases could not be measured with the installation available, but could only be roughly estimated from overall mass balances.

Fig. 11. SLV equilibrium in the NH_3–H_2O–NaOH system at 303 K and 0.7 MPa; initial concentration of NaOH, $w_{0,\,\mathrm{NaOH}} = 20$ mass %.

Table V. Temperature and Pressure of Observed SLVE

	NH_3–H_2O–NaOH		NH_3–H_2O–KOH	
T (K)	303	318	303	318
p (MPa)	0.7	1.1	0.6–0.7	1.1

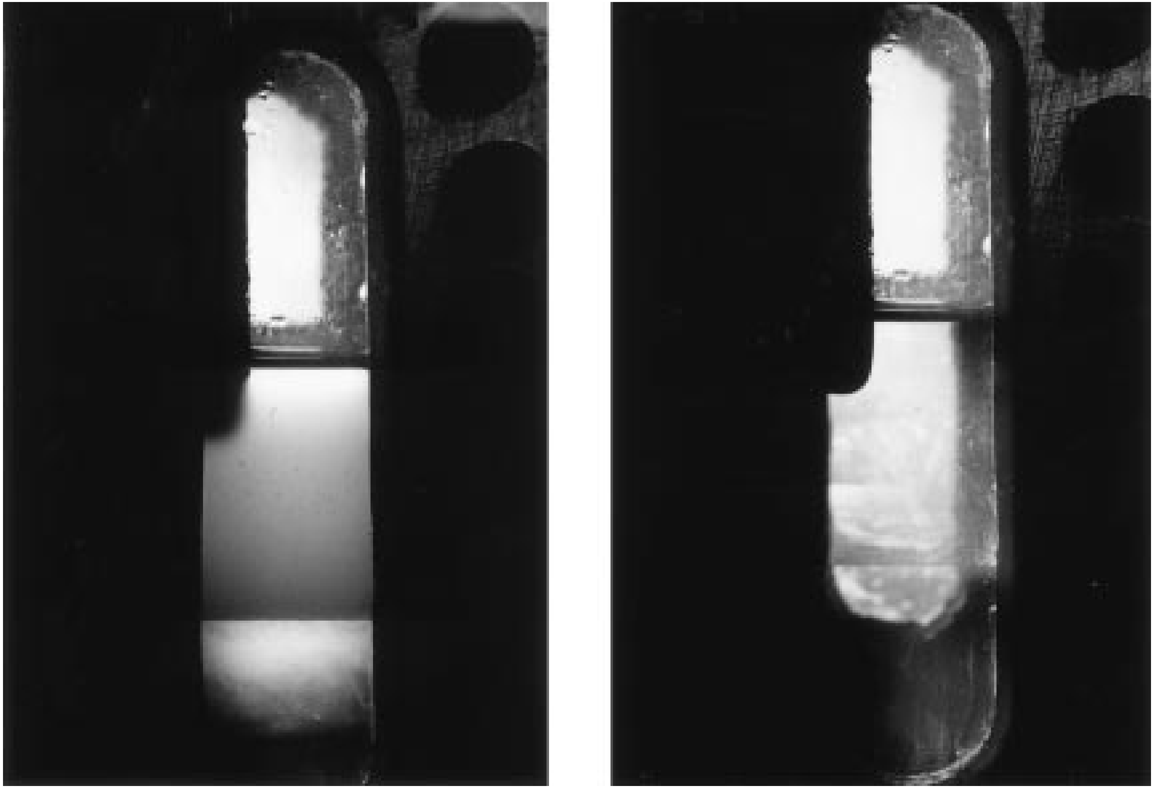

Fig. 12. LLV equilibrium in the NH_3–H_2O–KOH system at 318 K and 1.1 MPa; initial concentration of KOH, $w_{0,\,\mathrm{KOH}} = 40$ mass %.

Liquid–liquid–vapor equilibria (LLVE) were observed in the NH_3–H_2O–KOH system at 318 K and 1.1 MPa and at an initial concentration of KOH in water $w_{0,\,\mathrm{KOH}} = 40$ mass %. This three-phase state is depicted in Fig. 12, the left photo referring to a state where the liquid phase is continuously circulated around the liquid loop, and the right photo having been taken after shutdown of the recirculation pump.

An analytic model for correlation of the VLE data was proposed in Ref. 1. The model is based on a quasi-chemical reaction scheme for the liquid phase taking into account its electrolyte structure. The model may serve as a starting point for further developments, with the final goal of calculating all properties of interest in the ternary systems studied here.

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NOMENCLATURE

m	Mass (kg)
p	Pressure (MPa)
T	Temperature (K)
w	Mass fraction
$w_{0,\,\mathrm{MOH}}$	Mass fraction of salt MOH in the equilibrium cell at the beginning of the experiments; $w_{0,\,\mathrm{MOH}} = m_{\mathrm{MOH}}/(m_{\mathrm{MOH}} + m_{\mathrm{H_2O}})$, M = Na, K

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