Solid-Liquid Phase Equilibria in the System NH_4Cl—$MgCl_2$—H_2O at Elevated Temperatures
The Pseudobinary System $MgCl_2 \cdot 6H_2O$—NH_4Cl

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The solid-liquid phase equilibria of the pseudobinary system $MgCl_2$ $6H_2O$—NH_4Cl were determined in the temperature range 120—250 °C. Between 120—183 °C ammonium carnallite NH_4Cl $MgCl_2$ $6H_2O$ forms the stable solid phase, which melts congruently at 183 °C. At higher temperatures solid solutions of the composition $(NH_4Cl)_{6.65} \cdot MgCl_2 \cdot 2H_2O$ are stable. The $NH_4Cl/MgCl_2$ mole ratio of the solid solutions is almost independent of temperature, if the $H_2O/MgCl_2$ mole ratio of the liquid phase is kept constant.

In recent years, comprehensive investigations of the properties of salt—water systems at elevated temperatures were carried out. The stability of new double salt hydrates and of a solid solution series was detected for example in the system KCl—$MgCl_2$—H_2O [1—4]. Besides the solid-liquid phase equilibria the melting and decomposition behaviour of salt and double salt hydrates was determined.

For compounds of the carnallite type $ACl \cdot MgCl_2 \cdot 6H_2O$ with A = K^+, NH_4^+, Rb^+, Cs^+, congruent melting behaviour was deduced for the Rb- and Cs-carnallite with melting points at 193 and 152.5 °C, respectively, while $KCl \cdot MgCl_2 \cdot 6H_2O$ melts incongruently at 167 °C. As for ammonium carnallite the results of thermal analyses are not unambiguous. So it could not be decided whether NH_4Cl $MgCl_2$ $6H_2O$ melts congruently or incongruently [5, 6].

Information concerning the appropriate solid-liquid phase equilibria of the system NH_4Cl—$MgCl_2$—H_2O at elevated temperatures is not available. Only the subsystems NH_4Cl—H_2O [7] and $MgCl_2$—H_2O [2, 8] are known up to 400 and 250 °C, respectively.

Hence we investigated the solid-liquid phase equilibria of the pseudobinary system $MgCl_2 \cdot 6H_2O$—NH_4Cl in the temperature range 120—250 °C.

EXPERIMENTAL

An analytical method has been selected for the investigation of phase equilibria. The liquid phase and at least one solid phase is equilibrated at constant temperature in special teflon-lined autoclaves. In general 60 h are sufficient to attain equilibrium.

The liquid phase is separated from the solid phases by means of a high-temperature centrifuge, and the composition of each phase is determined by chemical analysis. The experimental method used and the accompanying experimental procedures are described in detail in previous publications [1—3], the employed methods of the quantitative analysis of the liquid and solid phases are given in Table 1.

Furthermore, X-ray diffractometry and sometimes thermoanalytical methods were used to characterize the solid phases.

RESULTS AND DISCUSSION

The experimental results are summarized in Table 2. Besides the composition of the liquid phase the composition of the filter residue is given in the table. The values of the composition of the solid phase are corrected for the adherent liquid phase and for the condensed water vapour.

In Fig. 1 the composition of the liquid phase is plotted at different temperatures. In the temperature range 140—180 °C $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ forms the stable solid phase while at higher temperatures solid solutions with variable $NH_4Cl/MgCl_2$ mole ratio are stable. The general composition of the

Table 1. Methods of the Quantitative Analysis of the Liquid and Solid Phases

Species	Method	Relative error e/%
Mg^{2+}	complexometric	± 0.2
Cl^-	argentometric with potentiometric indication of the equivalent point	± 0.2
NH_4^+	Kjeldahl (in most cases calculated *via* the relation of electric neutrality)	± 2.0
H_2O	Karl Fischer	± 0.3
OH^-	titrimetric	± 1.5

solid solutions is $(NH_4Cl)_x \cdot MgCl_2 \cdot 2H_2O$. At 250 °C the separated solid phases (filter residue) have lower water content than it would be expected for a solid phase with the $H_2O/MgCl_2$ mole ratio of 2. Hence at this temperature the border of the solid solution series is probably not a solid phase with $MgCl_2$ $2H_2O$ entities.

The figurative points of the solid solutions are outside the pseudobinary phase diagram. Hence in the temperature range 190—250 °C isotherms of the system $NH_4Cl—MgCl_2—H_2O$ within a small $MgCl_2$ concentration interval around 166.7 mol $MgCl_2$/1000 mol H_2O had to be determined. These isotherms were interpolated in order to get the NH_4Cl concentration of the liquid phase at the $H_2O/MgCl_2$ mole ratio of 6 (Fig. 1).

Table 2. Solid-Liquid Phase Equilibria of the System $NH_4Cl—MgCl_2—H_2O$

θ/°C	Composition of liquid phase: mol $MgCl_2$ / 1000 mol H_2O	2 mol NH_4Cl / 1000 mol H_2O	Composition of filter residue: $n(NH_4Cl)/n(MgCl_2)$	$n(H_2O)/n(MgCl_2)$	Composition of solid phase $NH_4Cl_x \cdot MgCl_2 \cdot nH_2O$: x	n
120	165.63	0.90	0.90	5.91	0.90	5.91
140	166.32	4.85	0.94	5.95	0.94	5.95
160	166.32	11.88	0.96	5.96	0.96	5.96
175	166.82	22.95	0.97	5.94	0.97	5.94
175	129.82	110.43	2.44	5.66		
180	165.31	31.77	0.98	5.97	0.98	5.97
180	164.28	31.92	0.97	6.01	0.97	6.01
180	167.25	32.86	0.97	6.00	0.97	6.00
190	174.63	96.10	6.61	2.14	6.82	2
190	167.16	101.66	6.83	2.04	6.88	2
190	148.62	115.15	17.96	2.40	19.49	2
190	120.63	128.43	130.42	0.74		
200	135.10	135.52	0	0		
200	137.37	135.37	21.85	2.70	24.90	2
200	137.97	135.79	20.82	2.66	23.53	2
200	144.99	134.50	21.74	2.21	22.64	2
200	146.56	129.58	13.50	1.87	13.19	2
200	152.29	120.13	9.76	2.31	10.35	2
200	157.43	120.22	8.14	1.98	8.10	2
200	159.94	125.02	8.26	2.00	8.25	2
200	160.44	123.43	8.05	2.02	8.08	2
200	164.86	121.21	7.29	1.88	7.12	2
200	165.97	121.17	7.39	2.27	7.82	2
200	168.95	115.70	6.39	2.08	6.50	2
200	172.24	112.44	5.60	2.07	5.68	2
200	173.19	109.17	5.11	2.12	5.23	2
200	177.49	103.16	5.66	2.16	5.86	2
200	178.04	107.82	4.98	2.36	5.39	2
200	180.04	97.40	4.88	2.24	5.11	2
200	181.69	100.77	5.34	2.10	5.47	2
200	181.80	102.35	4.64	2.05	4.68	2
200	183.42	98.88	4.78	2.13	4.93	2
200	183.59	103.04	4.40	2.19	4.60	2
210	145.86	148.66	12.97	2.12	13.24	2
210	148.41	145.12	11.86	2.16	12.22	2
210	153.25	140.71	9.46	2.08	9.56	2
210	160.59	133.23	7.74	2.04	7.79	2
210	165.34	130.81	6.67	2.24	6.98	2
210	170.18	128.28	6.13	2.14	6.30	2
210	171.59	124.12	5.77	2.17	5.97	2
230	155.84	180.96	11.06	1.48		
230	184.22	153.01	5.18	1.88	5.06	2
250	166.13	215.54	9.54	0.31		
250	166.17	227.47	33.30	1.40		

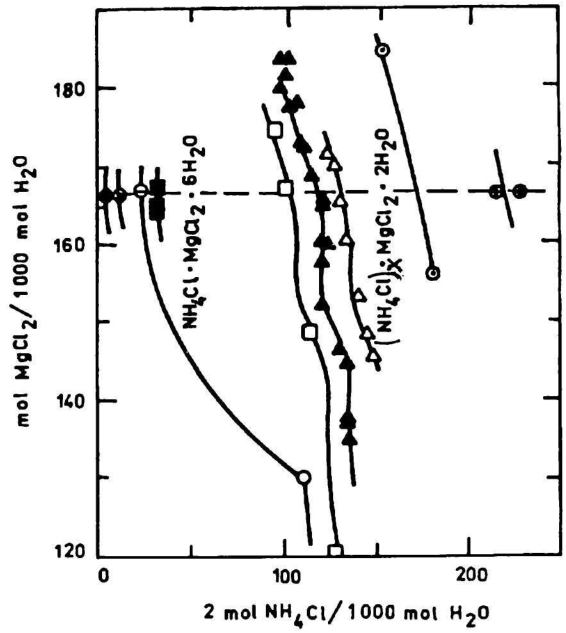

Fig. 1. Solid-liquid phase equilibria in the system NH_4Cl—$MgCl_2$—H_2O in the temperature range 120—250 °C. θ/°C: ○ 120, ● 140, ⊗ 160, ⊖ 175, ■180, □ 190, ▲ 200, Δ 210, ⊙ 230, ⊕ 250.

The phase diagrams of four different pseudobinary carnallite systems ACl—$MgCl_2$ $6H_2O$ with A = Rb, NH_4, K, and Cs are compared in Fig. 2. For the Rb system the congruent melting temperature of Rb-carnallite (193 °C) is known only from DTA experiments [5, 6]. So the liquidus of the Rb-carnallite plotted in Fig. 2 is a rough estimation.

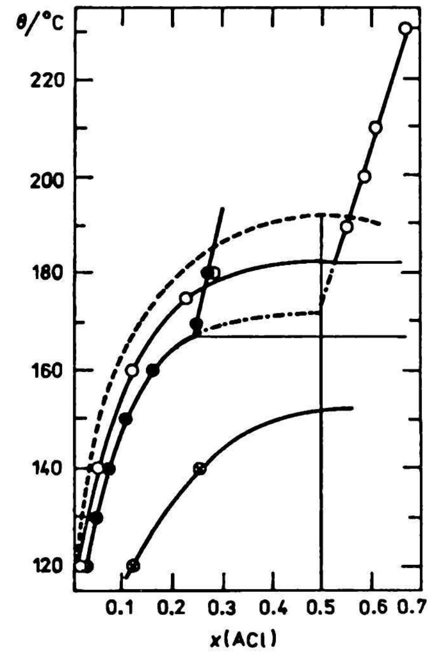

Fig. 2. Solid-liquid phase diagrams of the pseudobinary systems ACl—$MgCl_2 \cdot 6H_2O$ with A = Rb, NH_4, K, Cs in the temperature range 120—250 °C. - - - Rb, ○ NH_4, ● K, ⊗ Cs, -·- metastable.

The phase diagram of the K system was deduced from the solid-liquid phase equilibria of the appropriate ternary system KCl—$MgCl_2$—H_2O [1—4], and the Cs system [9] was investigated in a similar way as described for the NH_4 system.

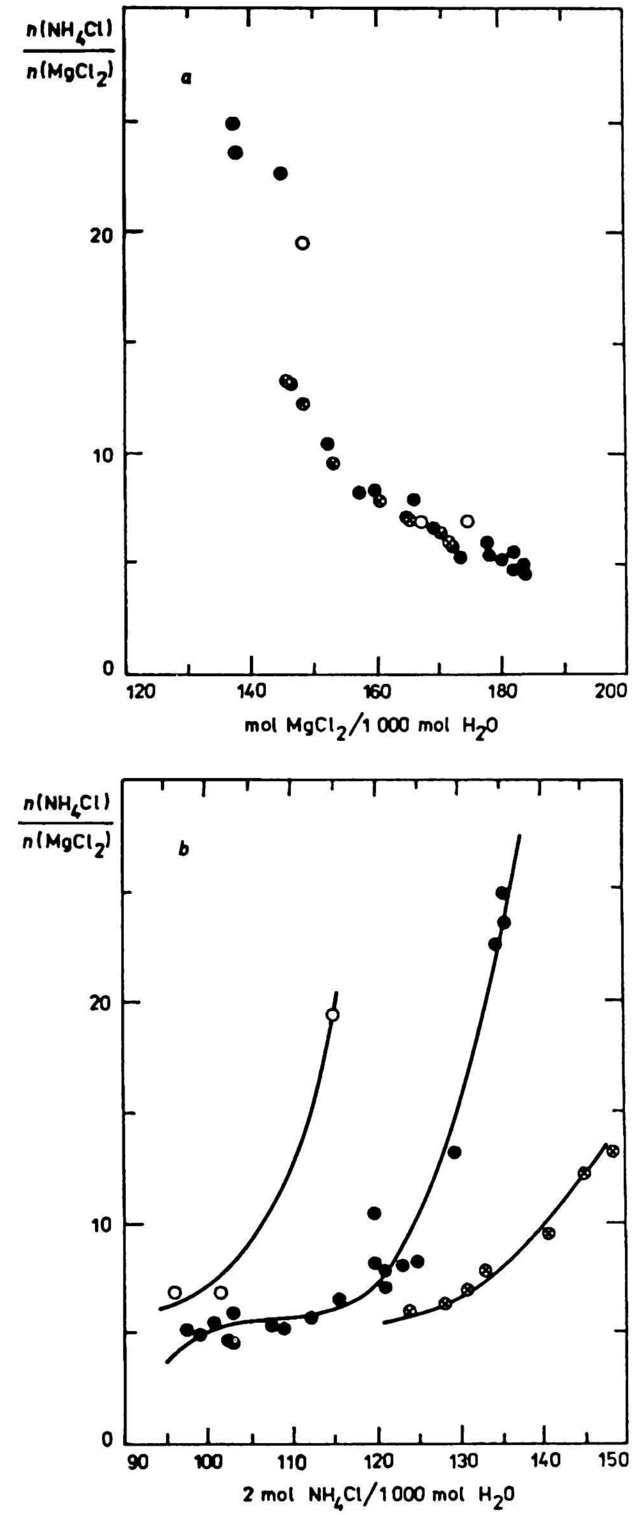

Fig. 3. Dependence of the $NH_4Cl/MgCl_2$ mole ratio x of the solid solutions $(NH_4Cl)_x \cdot MgCl_2 \cdot 2H_2O$ on the composition of the liquid phase at 190 (○), 200 (●), and 210 (⊗) °C.

By using an analytical method for the investigation of solid-liquid phase equilibria the direct determination of invariant points like a melting point of a double salt hydrate is not possible. To find out, whether NH_4Cl $MgCl_2$ $6H_2O$ melts congruently or incongruently the liquidus curves have to be extrapolated toward the melting temperature (193 °C) which is known from DTA experiments [5]. Extrapolation with respect to increasing temperature is not unambiguous because of the shape of the liquidus in the vicinity of the melting point (strong dependence of the composition on temperature). On the other hand, the liquidus curve of the solid solution is almost a straight line. Hence this liquidus can be extrapolated toward lower temperature. The extrapolation up to the mole fraction x(ACl) of 0.5 (composition of the carnallite) gives a temperature which is about 10 °C lower than the melting point (183 °C). Hence $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ melts congruently as shown in Fig. 2.

The composition of the solid solution mainly depends on the $MgCl_2$ concentration of the liquid phase and is almost independent of temperature. In Fig. 3 the $NH_4Cl/MgCl_2$ mole ratio of the solid solutions is plotted as a function of the composition of the liquid phase. At the $MgCl_2$ concentration of the liquid phase of 166.67 mol/1000 mol H_2O ($H_2O/MgCl_2$ mole ratio of 6) the following composition of the solid solutions at temperatures below 230 °C can be deduced

$$(NH_4Cl)_{6.65} \quad MgCl_2 \quad 2H_2O$$

One of the limiting states of the solid solution series is NH_4Cl. In particular at 200 °C, where a larger $MgCl_2$ concentration interval was investigated, an inflection point seems to appear at the $NH_4Cl/MgCl_2$ mole ratio of the solids of about 5 as can be seen in Fig. 3*b*. This gives a hint that $5NH_4Cl$ $MgCl_2$ $2H_2O$ could be the other limiting state of the solid solution series, or there exists complete miscibility between NH_4Cl and $MgCl_2$ $2H_2O$. In order to decide this question, a more detailed investigation of the phase diagram of the system $NH_4Cl—MgCl_2—H_2O$ is necessary.

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