EFFECT OF TEMPERATURE ON THE SOLUBILITY DIAGRAMS OF AMMONIUM BROMCARNALLITE

Christomir CHRISTOV and Christo BALAREW

Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

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The solubility isotherms of the systems NH_4Br–$MgBr_2$–H_2O and NH_4Br . $MgBr_2$. 6 H_2O–$MgBr_2$–H_2O have been investigated by the physicochemical analysis method at 75 °C and formation of carnallite type double salt is established. The effect of temperature on the crystallization conditions is discussed.

The ternary water–salt systems of the type MeX–MgX_2–H_2O) (Me = K, NH_4, Rb, Cs; X = Cl, Br) have been the subject of many studies. It is established that the solubility diagrams consist of three branches: a relatively wide crystallization field of the alkali halide, a crystallization field of the corresponding chlorcarnallite of bromcarnallite and a narrow field of MgX_2 . 6 H_2O (refs[1–6]). This can be explained by the pronounced trend of Mg^{2+} ions in halide systems to be coordinated with water molecules forming coordination polyhedra $[Mg(H_2O)_6]^{2+}$, which are a building unit of the crystalline salts MeX . MgX_2 . 6 H_2O. Due to the peculiarities of the Li^+ ion, based on its very small size, the salt LiCl . $MgCl_2$. 7 H_2O crystallizes in the LiCl–$MgCl_2$–H_2O system[7]. The salt is of the carnallite type again since the seventh water molecule is bound directly to Li^+ – $Li(H_2O)Cl$. $Mg(H_2O)_6Cl_2$ (ref.[8]). In the LiBr–$MgBr_2$–H_2O system there is no field of equilibrium crystallization of lithium bromcarnallite[9], which is attributed to the supposed higher solubility of this salt.

The NH_4Br–$MgBr_2$–H_2O system has been investigated within the temperature range of 0 – 50 °C and crystallization of incongruently water-soluble ammonium bromcarnallite has been established[4–6].

The subject of our studies are the systems NH_4Br–$MgBr_2$–H_2O and NH_4Br . $MgBr_2$. 6 H_2O–$MgBr_2$–H_2O at 75 °C for which there are no data in the literature.

The purpose is to establish the effect of temperature on the crystallization of ammonium bromcarnallite. The results from investigations on the solubility of the NH_4Br–$MgBr_2$–H_2O system over a wide temperature range are summarized.

EXPERIMENTAL

The solubility diagrams were investigated by isothermal decrease of the supersaturation[10]. All chemicals used, NH_4Br and $MgBr_2 . 6 H_2O$ were of analytical grade. Equilibrium was attained by continuous stirring for 12 h.

The compositions of the saturated solutions and the corresponding wet residua were determined by the following methods: ion NH^{4+} was determined by amperometric titration with 0.2 M sodium tetraphenylborate[11]. Ion Mg^{2+} was established by direct complexometric titration in an ammonium buffer (pH 9) with eryochrome black T as indicator[12]. Anion Br^- was determined argentometrically by the Mohr method. The compositions of the thoroughly suction dried solid phases (simple and double salts) were specified by the Schreinemakers' graphic method[13].

The ammonium bromcarnallite obtained was also identified thermogravimetrically with a Paulik–Paulik–Erdey[14] apparatus (type 3427) as samples of 200 mg which were placed in a corundum crucible and heated to 1 000 °C under air with a heating rate of 10 °C/min. The phase composition of $NH_4Br . MgBr_2 . 6 H_2O$ was controlled with a DRON-3 powder X-ray diffractometer (Co/CuKα radiation) at a recording rate of 2°/min.

RESULTS AND DISCUSSION

The results from the investigation on the $NH_4Br–MgBr_2–H_2O$ system at 75 °C are presented in Table I. Crystallization of congruently water-soluble ammonium bromcarnallite is established. The results on the system $NH_4Br . MgBr_2 . 6 H_2O–MgBr_2–H_2O$ at

TABLE I
Solubility in the $NH_4Br–MgBr_2–H_2O$ system at 75 °C

Liquid phase, wt.%		Wet residua, wt.%		Solid phase
NH_4Br	$MgBr_2$	NH_4Br	$MgBr_2$	
54.60	0.00	93.84	–	NH_4Br
43.85	10.88	89.82	2.03	NH_4Br
38.39	16.52	82.48	4.82	NH_4Br
28.90	25.08	78.08	7.86	NH_4Br
20.32	34.69	70.06	13.12	NH_4Br
19.78	36.50	31.22	39.14	eutonic
17.03	38.17	21.25	42.57	$NH_4Br . MgBr_2 . 6 H_2O$
14.08	39.82	23.26	47.06	$NH_4Br . MgBr_2 . 6 H_2O$
10.15	43.68	21.91	46.63	$NH_4Br . MgBr_2 . 6 H_2O$
4.12	48.64	18.94	47.72	$NH_4Br . MgBr_2 . 6 H_2O$
0.62	53.20	6.02	59.84	eutonic
0.00	53.50	–	62.11	$MgBr_2 . 6 H_2O$

75 °C are given in Table II. The system is found to be eutonic. The double salt NH_4Br . $MgBr_2$. 6 H_2O was studied thermogravimetrically. The sample weight decreases by 27.7% at 160 – 270 °C. This percentage corresponds to the theoretical content of crystallization water in the salt NH_4Br . $MgBr_2$. 6 H_2O. Table III shows the interplanar distances and the intensities obtained for ammonium bromcarnallite.

TABLE II
Solubility in the NH_4Br . $MgBr_2$. 6 H_2O–$MgBr_2$–H_2O system at 75 °C

Liquid phase, wt.%		Wet residue, wt.%		Solid phase
NH_4Br . $MgBr_2$	$MgBr_2$[a]	NH_4Br . $MgBr_2$	$MgBr_2$[a]	
56.74	0.00	71.20	–	NH_4Br . $MgBr_2$. 6 H_2O
45.22	7.08	68.82	2.08	NH_4Br . $MgBr_2$. 6 H_2O
21.34	28.05	59.86	7.10	NH_4Br . $MgBr_2$. 6 H_2O
17.78	32.54	58.04	8.85	NH_4Br . $MgBr_2$. 6 H_2O
8.22	43.48	42.75	19.68	NH_4Br . $MgBr_2$. 6 H_2O
4.38	47.92	57.26	10.85	NH_4Br . $MgBr_2$. 6 H_2O
1.88	52.02	4.22	55.08	eutonic
1.26	52.84	0.72	61.24	$MgBr_2$. 6 H_2O
0.00	53.50	–	61.76	$MgBr_2$. 6 H_2O

[a] $MgBr_2$ content in excess of the stoichiometric amount corresponding to NH_4Br . $MgBr_2$.

TABLE III
X-Ray patterns of the double salt NH_4Br . $MgBr_2$. 6 H_2O

d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
6.817	12	2.804	23	2.283	9
3.992	70	2.777	9	2.258	7
3.916	19	2.737	10	2.169	8
3.484	6	2.541	6	2.120	32
3.443	15	2.530	4	2.066	30
3.416	100	2.462	5	2.052	34
3.066	30	2.421	15	1.986	6
3.022	36	2.396	6	1.962	17

Comparison of the results obtained on the NH_4Br–$MgBr_2$–H_2O system at 0 °C (ref.[4]), 25 °C (refs[4,5]), 50 °C (ref.[6]) and 75 °C permits establishing the following relationships.

With rising temperature, the solubility of NH_4Br in the binary system increases more that of $MgBr_2 . 6 H_2O$. This difference and the effect of temperature on the solubility of the ammonium bromcarnallite formed has a decisive effect on the shape of the solubility isotherms of the ternary systems. Thus, with the increase in temperature from 0 °C to 75 °C, the crystallization field of NH_4Br is narrowed at the expense of a broadening of the double salt crystallization field. For that reason, ammonium bromcarnallite, which is incongruently soluble at 0 – 50 °C, becomes congruently soluble in water at 75 °C. With rising temperature from 50 to 75 °C, the solubility of $NH_4Br . MgBr_2 . 6 H_2O$ increases more strongly than is the case of $MgBr_2 . 6 H_2O$. This results in a very narrow crystallization field of $MgBr_2 . 6 H_2O$ in the solubility isotherm.

The congruent solubility of ammonium bromcarnallite at 75 °C allowed the study of the system $NH_4Br . MgBr_2 . 6 H_2O$–$MgBr_2$–H_2O at the same temperature. The results obtained have shown that the increase in magnesium bromide concentration is accompanied by a decrease in the double salt solubility. Finally, it can be concluded that the change in size of the crystallization field of each salt in the NH_4Br–$MgBr_2$–H_2O system with changing temperature can be attributed to the effect of temperature on the solubilities of the components (NH_4Br, $MgBr_2 . 6 H_2O$ and $NH_4Br . MgBr_2 . 6 H_2O$) of the ternary solution. It is established that ammonium bromcarnallite is “just congruent” at 75 °C (a temperature which is very close to the conversion temperature). This fact permits choosing of: (i) suitable conditions of isolation of $NH_4Br . MgBr_2 . 6 H_2O$ by isothermal evaporation of its saturated solution and (ii) appropriate temperatures for investigation of its co-crystallization with other carnallite type double salts.

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REFERENCES

1. Kurnakov N., Osokoreva N.: Kalii *2*, 27 (1932).
2. Voskresenskaya N.: Russ. J. Gen. Chem. *4*, 152 (1934).
3. D’Ans J., Busch F.: Z. Anorg. Allg. Chem. *232*, 337 (1937).
4. Bogoyavlenskii P., Fedunyak I.: Russ. J. Inorg. Chem. *17*, 228 (1972).
5. Balarew Ch., Christov Ch., Valyashko V., Petrenko S.: J. Solution Chem. *22*, 173 (1993).
6. Balarew Ch., Christov Ch.: C. R. Acad. Bulg. Sci. *45*, 49 (1992).
7. Voskresenskaya N., Janateva O.: Izv. Akad. Nauk USSR, Ser. Khim. *1*, 102 (1937).
8. Emons H., Brand P., Pohl T., Koehnke K.: Z. Anorg. Allg. Chem. *563*, 180 (1988).
9. Christov Ch., Balarew Ch., Petrenko S., Valyashko V.: J. Solution Chem., in press.
10. Balarew Ch., Karaivanova V., Oikova T.: Comm. Dept. Chem. Bulg. Acad. Sci. *3*, 637 (1970).
11. Kulev I., Stanev D.: Collect. Czech. Chem. Commun. *46*, 3183 (1981).
12. Schwarzenbach G., Flaschka H.: *Kompleksometricheskoe Titrirovanie*. Izd. Khimya, Moskva 1968.
13. Schreinemakers F.: Z. Phys. Chem. *11*, 76 (1893); *55*, 73 (1906).
14. Paulik F., Paulik J., Erdey L.: *Derivatograph, technicheskie osnovi*. Vengerskii optich. zavod, Budapest 1974.