ISOMORPHIC CO-CRYSTALLIZATION OF AMMONIUM AND RUBIDIUM BROMOCARNALLITES

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The solubility isotherm of the system $NH_4Br . MgBr_2 . 6 H_2O$–$RbBr . MgBr_2 . 6 H_2O$–H_2O has been investigated at 75 °C and formation of a continuous series of mixed crystals is established. The factors determining the values of the distribution coefficients of the components between the crystalline and liquid phases are discussed.

Natural carnallite deposits contain a considerable amount of rubidium and cesium. The study of the solubility diagrams of carnallite type double salts is of great practical importance as rubidium and cesium are obtained from natural carnallite deposits.

The systems of the type Me^+X^-–MgX_2^-–H_2O (Me^+ = K^+, NH_4^+, Rb^+, Cs^+; X^- = Cl^-, Br^-) have been subject of many investigations[1–6]. Formation of carnallite type double salts ($MeX . MgX_2 . 6 H_2O$) only is established. Most double salts chlorocarnallites, bromocarnallites and iodocarnallites are isostructural and crystallize in a monoclinic crystal system (space group *C2/c*). The only known exception is potassium chlorocarnallite which crystallizes in an orthorhombic crystal system (space group *P2/n2/n2/a*) (refs[7–9]). Lithium chlorocarnallite, $Li(H_2O)Cl . MgCl_2 . 6 H_2O$, due to its different composition, crystallizes in space group *C2/m* (ref.[7]). Fluorocarnallites are not known.

It is of interest to investigate the co-crystallization of isostructural carnallite type double salts with a view to elucidate the reason of formation of continuous or discontinuous series of mixed crystals and establishing the factors that determine the values of the distribution coefficients of the components between the crystalline and liquid phases.

EXPERIMENTAL

The system $NH_4Br . MgBr_2 . 6 H_2O$–$RbBr . MgBr_2 . 6 H_2O$–H_2O was investigated at 75 °C. The experimental temperature was chosen in order to ensure congruent solubility of the two double salts in water. In ref.[5] it is shown that t = 75 °C is a temperature very close to the conversion temperature (from incongruent to congruent solubility) of ammonium bromocarnallite. The congruent solubility of

this double salt has allowed investigation of the system $NH_4Br \cdot MgBr_2 \cdot 6\,H_2O–MgBr_2–H_2O$ at 75 °C (ref.[5]). In ref.[6] it has been established that $t = 50$ °C is a temperature very close to the conversion temperature of rubidium bromocarnallite. Summarized data on ternary carnallite type systems are presented in ref.[10]. It has been found that the increase of temperature favours the crystallization of the $RbBr \cdot MgBr_2 \cdot 6\,H_2O$ in the system $RbBr–MgBr_2–H_2O$.

The double salts were prepared preliminary from saturated solutions within the crystallization fields of the double salts of the corresponding ternary systems: $NH_4Br–MgBr_2–H_2O$ (ref.[5]) and $RbBr–MgBr_2–H_2O$ (ref.[6]). All chemicals used (NH_4Br, $RbBr$ and $MgBr_2 \cdot 6\,H_2O$) were of analytical grade. The systems were studied by the method of isothermal decrease of the supersaturation[11]. Equilibrium was attained under continuous stirring of the system for 12 h.

The composition of the saturated solutions and the corresponding wet solid phases as well as of the initial double salts were established using titrimetric methods, the accuracy of which was 0.1 – 0.2%. The Rb^+ was determined amperometrically by titration with 0.1 M sodium tetraphenylborate[12], NH_4^+ being first allowed to evolve as NH_3 during boiling of the solution in the presence of NaOH. Determination of Mg^{2+} was achieved by direct complexometric titration in an ammonium buffer (pH 9) with eryochrome black T as indicator[13]. The Br^- content was found argentometrically by the Mohr method.

Schreinemakers' graphic method[14] for determination of the composition of the thoroughly suction-dried solid phases is applicable only in cases of crystallization of stoichiometric compounds – pure salts (anhydrous or crystalline hydrates) and double salts. In cases of mixed crystals formation, each change in the composition of the liquid phase inevitably changes the composition of the crystalline phase being in equilibrium with the liquid. For the crystallization of mixed crystals we have used the variation of Schreinemakers' method for algebraic indirect identification of the solid phase composition[15]. In this way we have determined the real composition of the thoroughly suction-dried mixed crystals by algebraic calculation using the results of experimental chemical determination of composition of the liquid and the corresponding wet solid phases.

Water content was determined thermogravimetrically with a Paulik–Paulik–Erdey 1500, type 3427 apparatus[16] upon heating to 500 °C. The phase composition of some mixed crystals, obtained from the $NH_4Br \cdot MgBr_2 \cdot 6\,H_2O–RbBr \cdot MgBr_2 \cdot 6\,H_2O–H_2O$ system, was controlled by a DRON-3 powder X-ray diffractometer (Co/Kα radiation) at a recording rate of 2 °/min.

RESULTS AND DISCUSSION

The results from the investigation on the $NH_4Br \cdot MgBr_2 \cdot 6\,H_2O–RbBr \cdot MgBr_2 \cdot 6\,H_2O–H_2O$ system are presented in Table I and Fig. 1. The data present the arithmetical mean of 3 parallel determinations.

Figure 2 shows the X-ray data on some solid phases obtained from the system. Formation of continuous series of mixed crystals is established. The experimentally obtained distribution coefficient of the components between the mixed crystal phase and the solution ($\overline{D}_{Rb^+/NH_4^+} = 0.80$) is in good agreement with the theoretically calculated $D^{th}_{Rb^+/NH_4^+}$ using the equation of isomorphic co-crystallization for ideal mixed crystals[1]COLUMNS(9), DIMENSION(IN), COLWIDTHS(E1,E1,.1183,E1,E1,.1183,E1,E1,E1), ABOVE(.0972), BELOW(.0972), HGUTTER(.0555), VGUTTER(.0555), KEEP(OFF), L1(R0C0..R0C9), L1(R2C0..R2C9), L1(R1C0..R1C2), L1(R1C3..R1C5), L1(R1C6..R1C8), L1(R11C0..R11C9)

$$D_{2/1}^{th} = \left(\frac{M_{1,0}}{M_{2,0}}\right)^2 . \tag{1}$$

Here, $M_{1,0}$ and $M_{2,0}$ are the solubilities of the pure double salts (in mol/1 000 g H_2O). A value of $D_{Rb^+/NH_4^+}^{th} = 0.89$ is obtained. This indicates that the mixed crystals formed by the above double salts are close to the ideal. The experimentally found distribution coefficients (D_{Rb^+/NH_4^+}, Table I) show the $NH_4Br . MgBr_2 . 6 H_2O$ based mixed crystals to be most close to the ideal crystals.

TABLE I
Solubility in the $NH_4Br . MgBr_2 . 6 H_2O$–$RbBr . MgBr_2 . 6 H_2O$–H_2O system at 75 °C; 1 $NH_4Br . MgBr_2$; 2 $RbBr . MgBr_2$

Liquid phase, wt.%		Wet solid phase, wt.%		Solid phase[a], wt.%		D_{Rb^+/NH_4^+}
1	2	1	2	1	2	
56.7	0.00	–	–	72.3	0.00	–
49.8	4.92	65.4	5.88	66.6	5.96	0.91
42.9	10.4	59.8	13.1	59.9	13.1	0.90
31.8	22.7	46.1	26.2	47.3	26.5	0.78
22.1	33.5	33.8	39.7	34.5	40.1	0.77
12.6	44.8	20.7	53.6	21.1	54.1	0.72
6.11	53.9	10.2	64.6	10.5	65.4	0.71
0.00	63.2	–	–	0.00	76.4	–
						$\overline{D} = 0.80$

[a] Calculated as thoroughly suction-dried.
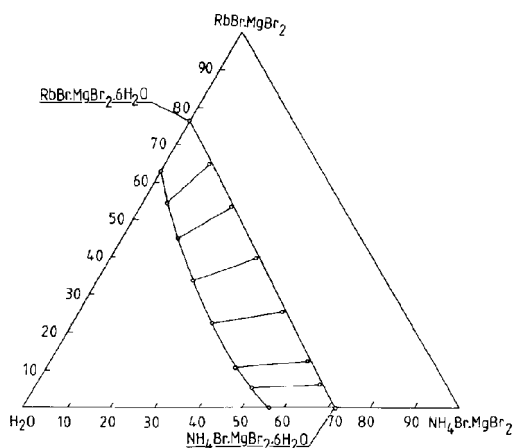
Fig. 1
Solubility diagram of the $NH_4Br . MgBr_2 . 6 H_2O$–$RbBr . MgBr_2 . 6 H_2O$–H_2O system at 75 °C (in wt.%)

The crystal structures of the carnallite type double salts are built up of two kinds of coordination polyhedra: $[Mg(H_2O)_6]$ and $[Me^+X_6]$. The different kinds of bonding of the $[Me^+X_6]$ octahedra determine the isodimorphism of these salts, i.e. the presence of carnallite and perovskite type structures[7,9]. Only $KCl . MgCl_2 . 6 H_2O$ has a carnallite type structure. All the other salts of the type $Me^+X . MgX_2 . 6 H_2O$ possess a perovskite structure. The isodimorphism of potassium and rubidium chlorocarnallites[18,19] and potassium and ammonium chlorocarnallites[20] is the reason of the formation of a discontinuous series of mixed crystals. The isostructure of the remaining carnallite type salts may be expected to lead to the formation of continuous series of mixed crystals. This has been confirmed by a study on the co-crystallization of ammonium and rubidium as well as ammonium and cesium chlorocarnallites[21] and ammonium and rubidium bromocarnallites (this study).

In all the three systems, where isomorphic co-crystallization occurs, the experimental values of the distribution coefficients are in very good agreement with those theoretically found (Table II) using Eq. (*1*). This indicates that: (i) the mixed crystals obtained

TABLE II
Experimental and theoretical values of the distribution coefficients D

System			$t, °C$	$\overline{D}_{1/2}$	$D^{th}_{1/2}$
component 1	component 2	water			
$RbBr . MgBr_2 . 6 H_2O$	$NH_4 . MgBr_2 . 6 H_2O$	H_2O	75	0.80	0.89
$NH_4Cl . MgCl_2 . 6 H_2O$	$RbCl . MgCl_2 . 6 H_2O$	H_2O^a	50	0.83	0.83
$CsCl . MgCl_2 . 6 H_2O$	$NH_4Cl. MgCl_2 . 6 H_2O$	H_2O^a	50	0.48	0.48

a From ref.[21].
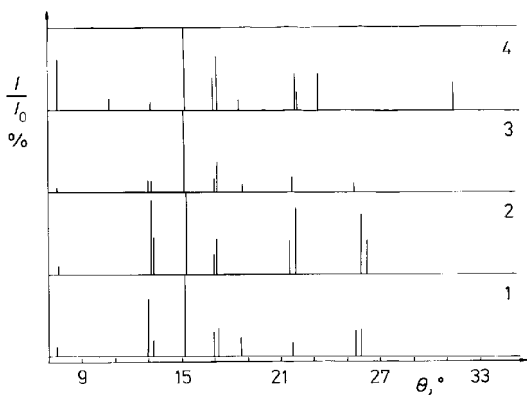
FIG. 2
Powder X-ray diffraction patterns of solid phases obtained from the $NH_4Br . MgBr_2 . 6 H_2O$–$RbBr . MgBr_2 . 6 H_2O$–H_2O system at 75 °C. 1 $NH_4Br . MgBr_2 . 6 H_2O$; 2 $(NH_4)_xRb_{1−x}Br . MgBr_2 . 6 H_2O$ (59.9% $NH_4Br . MgBr_2$, 13.1% $RbBr . MgBr_2$); 3 $(NH_4)_xRb_{1−x}Br . MgBr_2 . 6 H_2O$ (21.1% $NH_4Br . MgBr_2$, 54.1% $RbBr . MgBr_2$); 4 $RbBr . MgBr_2 . 6 H_2O$

from these pairs of salts are close to the ideal; (ii) the properties of the ternary solutions are additive with respect to the binary solutions of carnallite type double salts, i.e. the ionic forms in the solutions do not change. The Mg^{2+} ions exist mainly (both before and after mixing the binary solutions) as hexaaqua complexes $[Mg(H_2O)_6]^{2+}$. A series of authors have proved that after mixing alkali halide solutions, the additivity of the properties is preserved with a satisfactory accuracy[22–24]. The presence of additivity in the properties of carnallite type mixed solutions permits calculating, on the basis of Eq. (*1*), the distribution coefficients $D_{2/1}$ in cases of isomorphic co-crystallization.

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