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The Double Salt $RbCl \cdot NiCl_2 \cdot 2H_2O$

CHR. BALAREW, S. TEPAVITCHAROVA, AND J. MACICEK*

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria, and *Institute of Applied Mineralogy, Bulgarian Academy of Sciences, 1000 Sofia, Bulgaria*

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A study of the $RbCl–NiCl_2–H_2O$ system revealed the existence of the double salt $RbCl \cdot NiCl_2 \cdot 2H_2O$ at 50 and 75°C. In the temperature range 25–75°C the congruently soluble salt is $2RbCl \cdot NiCl_2 \cdot 2H_2O$. The salt $RbCl \cdot NiCl_2 \cdot 2H_2O$ does not appear at 25°C. It shows a relatively narrow crystallization field at 50°C, which is considerably broadened at 75°C. The thermal behavior of $RbCl \cdot NiCl_2 \cdot 2H_2O$ and $2RbCl \cdot NiCl_2 \cdot 2H_2O$ has been studied by DT analysis.

Introduction

The crystal structure (*1*) and some magnetic characteristics (*2*) of the $2RbCl \cdot NiCl_2 \cdot 2H_2O$ double salt have been described. This double salt is obtained by slow evaporation of an aqueous solution of RbCl and $NiCl_2 \cdot 6H_2O$ in stoichiometric amounts (*2*). Data for the mixed crystals $RbCl \cdot (Fe_{0.5}Ni_{0.5})Cl_2 \cdot 2H_2O$ isostructural with $RbCl \cdot FeCl_2 \cdot 2H_2O$ have been reported (*3*). The high degree of substitution of the Fe^{2+} ions for Ni^{2+} ions suggests that conditions should exist at which the double salt $RbCl \cdot NiCl_2 \cdot 2H_2O$ can be obtained as a separate phase.

With the aim of finding the conditions under which the salts $2RbCl \cdot NiCl_2 \cdot 2H_2O$ and $RbCl \cdot NiCl_2 \cdot 2H_2O$ crystallize from the $RbCl–NiCl_2–H_2O$ system, we have studied it within the temperature range 25–75°C.

Experimental

Synthesis

The system was studied by the solubility method using isothermal decrease of supersaturation (*4*). Equilibrium was attained by continuous stirring for 2 days at 25°C and 5–6 hr at 50 and 75°C. Experiments were carried out with MERCK analytical grade reagents. Compositions of the solid phases, considered as thoroughly suction dried, were determined graphically by Schreinemakers' method (*5*).

Chemical Analysis

The following analytical methods were used for the determination of the liquid and the corresponding wet solid phases:

Ni^{2+} was determined complexometrically by back titration in an acetate buffer, with xylenol orange as the indicator. The total amount of chloride was determined argentometrically, while RbCl content was evaluated as the difference between the total amount of chloride and the chlorides corresponding to the Ni^{2+} ions.

Thermogravimetric Analysis

The double salts were investigated thermogravimetrically with a Paulik-Paulik-Erdey 1500 apparatus, Type 3427, under the following conditions: weight of the sample

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was 400 mg; heating of the sample in air atmosphere at temperatures 600–650°C was at the rate of 10°C min^{-1}; sensitivity was $\frac{1}{200}$ mg.

X-ray Measurements

Determination of the phase composition of the samples obtained was carried out with a X-ray powder diffractometer DRON-3 using Co$K\alpha$ radiation with a β filter, a scintillation detector, and a scanning speed of 2°/min.

Unit cell parameters of the synthesized single crystals were determined on a Enraf-Nonius CAD-4 diffractometer (Mo$K\alpha$ radiation, graphite monochromator) from 25 well-centered reflections within the range $20° \leq \theta \leq 22°$.

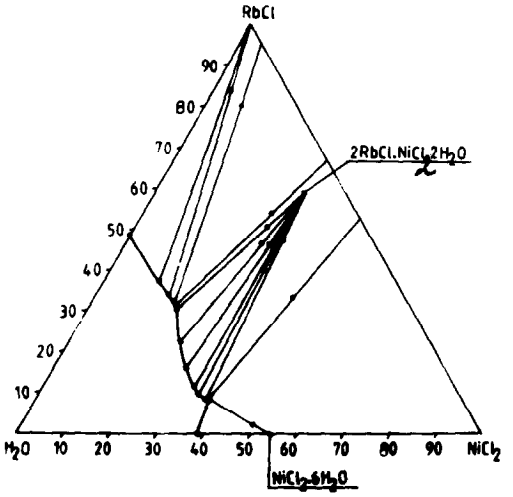

FIG. 1. Solubility diagram of the RbCl–$NiCl_2$–H_2O system at 25°C (in mass %).

Results and Discussion

Table I and Fig. 1 show the results obtained during the investigation of the RbCl–$NiCl_2$–H_2O system at 25°C. The solubility isotherm consists of three crystallization fields, corresponding to pure RbCl, to $NiCl_2 \cdot 6H_2O$, and to the double salt $2RbCl \cdot NiCl_2 \cdot 2H_2O$.

TABLE I

SOLUBILITY IN THE RbCl–$NiCl_2$–H_2O SYSTEM AT 25°C

Liquid phase (mass %)		Wet solid phase (mass %)		
$NiCl_2$	RbCl	$NiCl_2$	RbCl	Solid phase
0.00	48.60	—	—	RbCl
11.88	37.19	1.08	96.07	RbCl
15.52	34.17	3.98	83.89	RbCl
17.53	32.61	7.68	80.66	Eutonic
18.18	31.68	27.25	54.10	Eutonic
19.00	30.54	28.19	51.05	$2RbCl \cdot NiCl_2 \cdot 2H_2O$
24.00	22.75	29.12	46.82	$2RbCl \cdot NiCl_2 \cdot 2H_2O$
28.39	16.22	31.01	46.17	$2RbCl \cdot NiCl_2 \cdot 2H_2O$
32.34	11.89	31.98	46.67	$2RbCl \cdot NiCl_2 \cdot 2H_2O$
34.10	9.86	32.59	40.19	$2RbCl \cdot NiCl_2 \cdot 2H_2O$
36.71	8.30	33.49	47.42	$2RbCl \cdot NiCl_2 \cdot 2H_2O$
37.30	8.21	42.53	33.67	Eutonic
37.97	8.12	49.52	2.52	$NiCl_2 \cdot 6H_2O$
39.00	0.00	—	—	$NiCl_2 \cdot 6H_2O$

Investigations of the RbCl–$NiCl_2$–H_2O system at 50°C (Table II and Fig. 2), and at 75°C (Table III and Fig. 3), have shown that the solubility isotherms consist of four branches each. Along with the crystallization fields of the pure salts RbCl and $NiCl_2 \cdot 4H_2O$ at 50°C or $NiCl_2 \cdot 2H_2O$ at 75°C, respectively, as well as the double salt $2RbCl \cdot NiCl_2 \cdot 2H_2O$, existing at 25°C and congruently soluble at all three mentioned temperatures, a crystallization field of still another incongruently soluble double salt, $RbCl \cdot NiCl_2 \cdot 2H_2O$ (1 : 1 : 2), appears. This field has not hitherto been described in the literature. At 50°C a relatively narrow crystallization field corresponds to the double salt 1 : 1 : 2, which is considerably broadened at 75°C at the expense of the 2 : 1 : 2 double salt.

The double salts have been charaterized by DT and X-ray analyses in addition to the solubility diagrams and analytical methods.

Figure 4 shows DT analysis data for the double salt $2RbCl \cdot NiCl_2 \cdot 2H_2O$. The decrease in the weight of the sample by 8.5

TABLE II

SOLUBILITY IN THE RbCl–$NiCl_2$–H_2O SYSTEM AT 50°C

Liquid phase (mass %)		Wet solid phase (mass %)		
$NiCl_2$	RbCl	$NiCl_2$	RbCl	Solid phase
0.00	52.20	—	—	RbCl
6.89	46.42	0.08	96.41	RbCl
10.36	44.38	0.30	99.01	RbCl
12.17	44.42	0.55	97.50	RbCl
14.26	43.72	4.10	85.42	Eutonic
16.21	37.32	26.98	54.18	2RbCl · $NiCl_2$ · $2H_2O$
28.93	18.15	30.54	46.46	2RbCl · $NiCl_2$ · $2H_2O$
32.77	14.21	32.38	38.25	2RbCl · $NiCl_2$ · $2H_2O$
34.64	11.97	32.00	56.90	2RbCl · $NiCl_2$ · $2H_2O$
39.20	8.80	40.62	43.71	Eutonic
39.19	8.70	42.71	33.81	Eutonic
40.34	7.24	43.76	32.11	RbCl · $NiCl_2$ · $2H_2O$
41.30	5.98	44.63	42.20	RbCl · $NiCl_2$ · $2H_2O$
42.38	4.25	44.99	36.01	RbCl · $NiCl_2$ · $2H_2O$
43.33	3.77	46.27	29.33	Eutonic
42.92	3.10	46.24	13.88	Eutonic
43.14	2.50	57.19	0.89	$NiCl_2$ · $4H_2O$
43.22	0.00	—	—	$NiCl_2$ · $4H_2O$

TABLE III

SOLUBILITY IN THE RbCl–$NiCl_2$–H_2O SYSTEM AT 75°C

Liquid phase (mass %)		Wet solid phase (mass %)		
$NiCl_2$	RbCl	$NiCl_2$	RbCl	Solid phase
0.00	56.61	0.00	92.02	RbCl
9.35	47.65	0.56	97.42	RbCl
11.09	47.04	18.43	65.91	Eutonic
11.12	46.85	24.21	56.00	Eutonic
14.68	41.00	27.20	54.12	2RbCl · $NiCl_2$ · $2H_2O$
28.60	23.39	31.08	49.72	2RbCl · $NiCl_2$ · $2H_2O$
31.10	21.00	31.68	44.34	2RbCl · $NiCl_2$ · $2H_2O$
32.03	20.27	38.89	41.37	Eutonic
32.88	19.21	44.32	39.40	RbCl · $NiCl_2$ · $2H_2O$
34.08	17.73	45.87	41.07	RbCl · $NiCl_2$ · $2H_2O$
37.82	12.81	44.83	36.93	RbCl · $NiCl_2$ · $2H_2O$
40.42	10.04	44.96	37.53	RbCl · $NiCl_2$ · $2H_2O$
40.94	9.38	45.22	38.37	RbCl · $NiCl_2$ · $2H_2O$
43.05	6.37	45.81	42.10	RbCl · $NiCl_2$ · $2H_2O$
44.93	4.88	45.32	29.41	RbCl · $NiCl_2$ · $2H_2O$
46.60	2.46	53.22	31.91	Eutonic
47.21	0.00	69.92	0.00	$NiCl_2$ · $2H_2O$

wt% within the temperature range 120–160°C corresponds to the theoretically calculated crystalline water in the salt. The second endothermic peak of the DTA curve at 470°C is due to the melting of the anhydrous double salt.

Single crystals of the double salt 2RbCl · $NiCl_2$ · $2H_2O$ suitable for X-ray analysis were prepared at 25°C by slow evaporation of a saturated solution containing RbCl and $NiCl_2$, in a ratio defined by the crystallization field of this double salt and determined

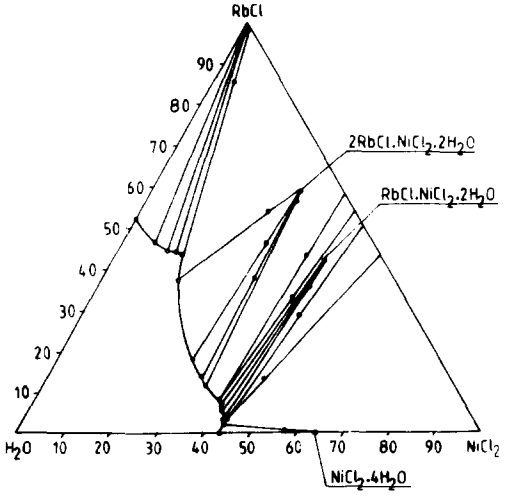

FIG. 2. Solubility diagram of the RbCl–$NiCl_2$–H_2O system at 50°C (in mass %).

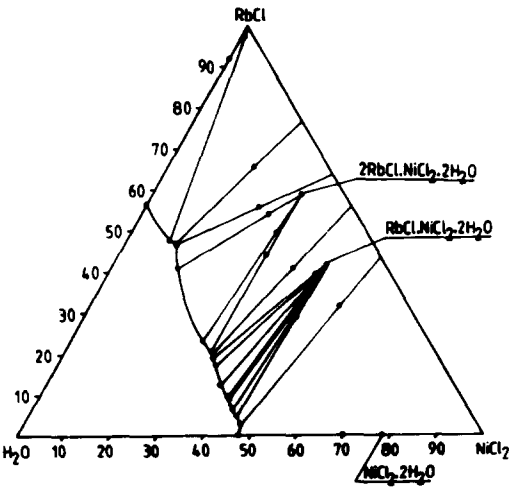

FIG. 3. Solubility diagram of the RbCl–$NiCl_2$–H_2O system at 75°C (in mass %).

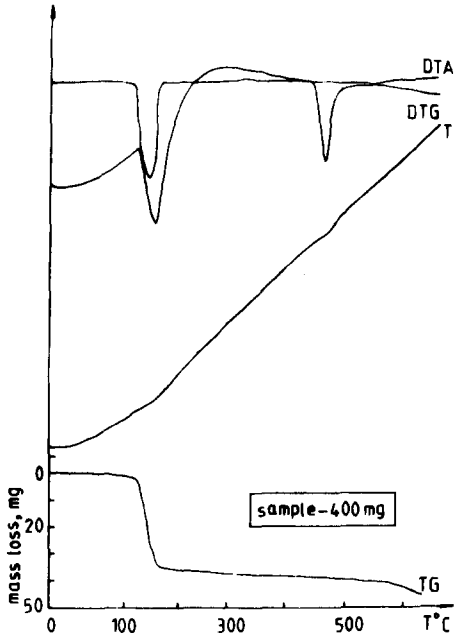

FIG. 4. DTA and TG data for the double salt $2RbCl \cdot NiCl_2 \cdot 2H_2O$. Paulik–Paulik–Erdey 1500 apparatus, Type 3427; heating rate 10°C min^{-1}.

by the investigation of the $RbCl–NiCl_2–H_2O$ system at 25°C. The crystals are yellow with a rhombic habitus. The double salt $2RbCl \cdot NiCl_2 \cdot 2H_2O$ crystallizes in the triclinic crystal system having unit cell parameters a = 5.569(1) Å, b = 6.448(1) Å, c = 6.970(2) Å, α = 65.48(2)°, β = 87.48(1)°, γ = 84.13(1)°, W = 226.5 Å^3, Z = 1, d_x = 2.987 g cm^{-3}, space group $P\bar{1}$. These results are in very good agreement with the data in (*2*).

The crystalline water content of the double salt $RbCl \cdot NiCl_2 \cdot 2H_2O$ was determined by the Karl-Fischer method (12.35 wt%) and by DT analysis (Fig. 5). The figure shows a decrease in the weight of the sample by 12.5 wt% within the temperature range 60–200°C, due to dehydration of the double salt. The endothermic effect at 420°C is related to the melting of the dehydrated product.

The results of both analyses provide evidence for the presence of two water molecules in the composition of the double salt. However, all attempts to grow single crystals suitable for determination of the unit cell parameters of this double salt failed. The X-ray powder diffraction of crystals obtained by the slow evaporation of appropriate aqueous solutions of RbCl and $NiCl_2$ at 50°C has shown the following parameters of a hexagonal lattice: a = 6.955(1) Å, c = 5.904(2) Å.

This result fits well with the unit cell parameters of the dehydrated $RbCl \cdot NiCl_2$ salt, obtained by Asmussen *et al.* (*6*). Such a coincidence is rather unexpected, since these authors describe a specific method for its preparation (under dry conditions), in an effort to eliminate the possible hydration of the salt.

The problem concerning the preparation of single crystals and the determination of

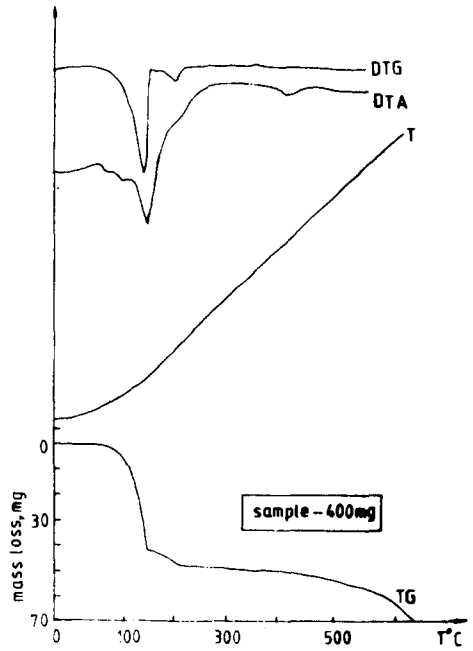

FIG. 5. DTA and TG data for the double salt $RbCl \cdot NiCl_2 \cdot 2H_2O$. Paulik–Paulik–Erdey 1500 apparatus, Type 3427; heating rate 10°C min^{-1}.

the crystal structure of the double salt RbCl · $NiCl_2$ ·$2H_2O$ still remains.

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