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QUATERNARY COMPOUNDS IN THE SYSTEM $KCl/NaCl/MgCl_2$?

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ABSTRACT

In the ternary system $KCl/NaCl/MgCl_2$ an incongruently melting compound $K_3NaMgCl_6$ exists with the peritectic at 743K. It crystallizes in the hexagonal structure with a=1201 and c=1387pm. The analogous compounds K_3NaMCl_6 (M=Fe, Mn, V, Cd) are isotypic. The existence of the compound $0.5NaCl \cdot KCl \cdot MgCl_2$ could not be confirmed.

INTRODUCTION

By the reinvestigation of the binary system $KCl/MgCl_2$ the compound K_4MgCl_6 (ref.1) was found, which crystallizes with the K_4CdCl_6-structure (ref.2). In this type three K^+-ions with the coordination number C.N.=8 and one K^+-ion with C.N.=6 occupy two different positions. Thus a K^+-ion can probably be replaced by a Na^+-ion. The first known representative of such a group of compounds is $K_3NaFeCl_6$ (ref.3), for which however the K^+-parameters were incorrectly (ref.2) stated.

A reference to such a compound should expose the line HO (fig.1) in the phase diagram of the already investigated system $KCl/NaCl/MgCl_2$ (ref.4); this line was confirmed later on (ref.5), but not correctly explained. (The analogous line is contained in the corresponding Mn-system (ref.6)). But it must be noticed, that the ternary system is incomplete in consequence of missing compounds in the binary systems. These are the compounds K_4MgCl_6, K_2MgCl_4, $K_3Mg_2Cl_7$ in the system $KCl/MgCl_2$ (ref.1) and Na_6MgCl_8, $NaMgCl_3$ and $Na_2Mg_3Cl_8$ instead of $NaMg_2Cl_5$ in the system $NaCl/MgCl_2$ (ref.7). Recently Russian scientists (ref.8) mentioned an additional quaternary compound $0.5NaCl \cdot KCl \cdot MgCl_2$. This compound is not contained in the section $KMgCl_3/NaCl$ (fig. 1).

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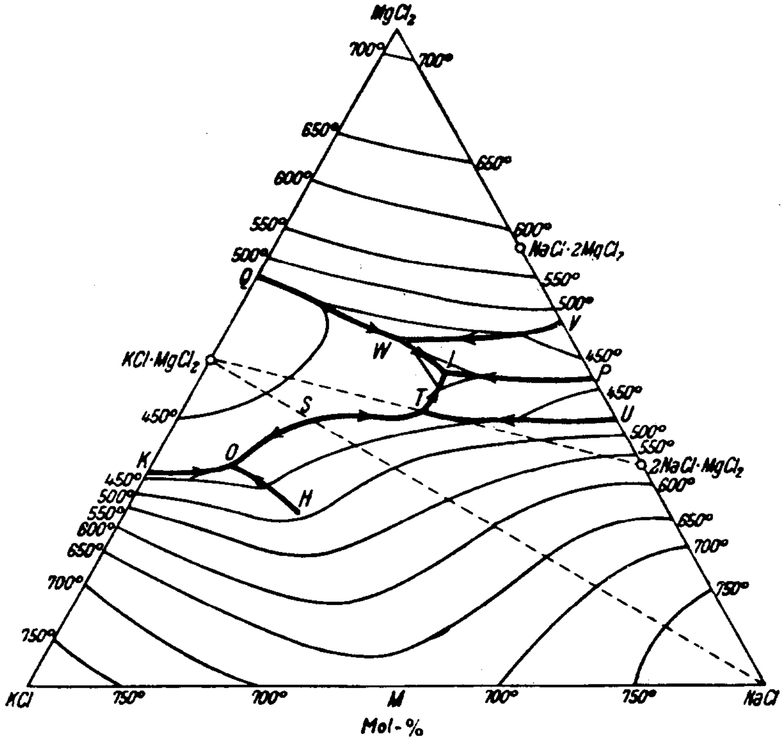

Fig. 1. System $KCl/NaCl/MgCl_2$ (ref.4)

EXPERIMENTAL

$MgCl_2$ was prepared by gradual heating of $NH_4MgCl_3 \cdot 6H_2O$ in a HCl-stream up to the melting point; KCl and NaCl were dried in a HCl-stream at 500^oC. DTA-samples were melted in sealed quartz ampoules. - Powder patterns were taken using a goniometer equipped with a vacuum attachment. High-temperature patterns at varying temperatures were measured with a Simon-Guinier-camera. The galvanic cell for e.m.f.-measurements on solid electrolytes was previously described (ref.9).

RESULTS AND DISCUSSION

The existence of a compound $0.5NaCl \cdot KCl \cdot MgCl_2$

A quasibinary section in a ternary system forms a simple eutectic system only when the saddlepoint lies exactly on the section. Small divergence may lead to a false interpretation. This occurs in the case of the section $KMgCl_3/NaCl$, which is obviously almost quasibinary, as can be seen in the phase diagram determined by DTA

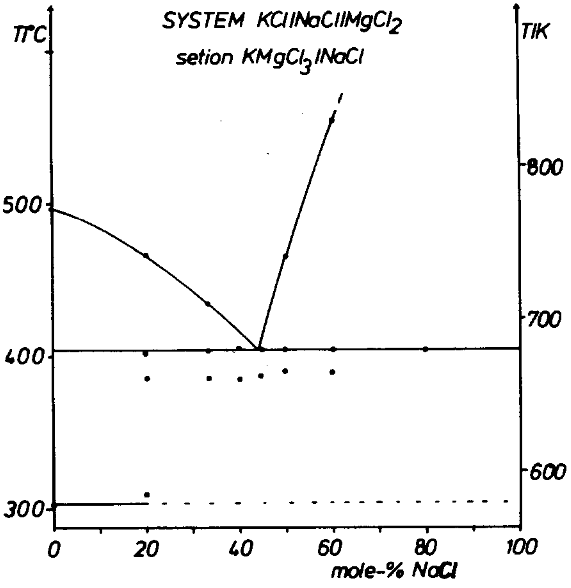

Fig. 2. System $KMgCl_3/NaCl$

(fig. 2): Below the strong eutectic effect at 678K there is a relatively weak thermal effect, which could belong to the ternary eutectic point I (fig. 1). (The effect at 578K is due to a phase transition of $KMgCl_3$.)

X-ray investigations confirm this observation. Diffractometerdiagrams of the DTA-samples and the high-temperature Guinier-diagram, especially of the sample with $0.5NaCl/KCl/MgCl_2$ up to 400°C, consist only of the $KMgCl_3$ - and NaCl-reflections.

In fig. 3 a part of the Guinier-diagram is given.

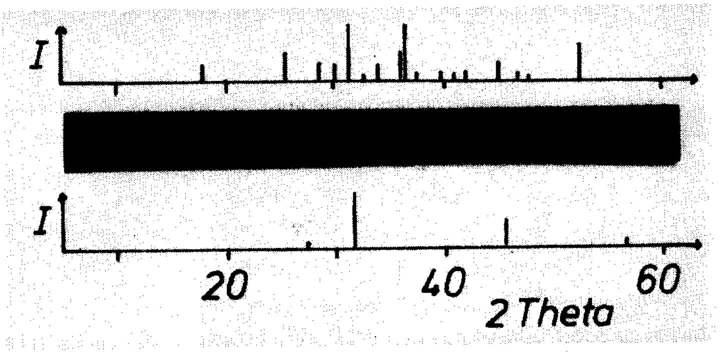

Fig. 3. Guinier-diagram of '$0.5NaCl \cdot KCl \cdot MgCl_2$' (middle), X-ray-reflections of $KMgCl_3$ (above) and NaCl (below)(all CuKα).

The existence of the compound $K_3NaMgCl_6$

Thermal effects of some samples of the section $KCl/NaMgCl_3$ are listed in table 1. The temperatures from cooling curves are given in each case in the upper line, and from heating curves taken after annealing below. The omission of the thermal effect at 400° in the heating curves with 20 and 25% is due to the incongruently melting compound $K_3NaMgCl_6$ with the peritectic at ~ 470°C.

Table 1. Thermal effects measured by DTA.

mole-% $NaMgCl_3$	T/°C		
20	591	426	408
	597	466	-
25	541	449	402
	545	470	-
30	499	439	397
	-	471	398

The stable phases in the solid state on the section $KCl/NaMgCl_3$ are:

0		25		50		54.6		66.7		mole%-$NaMgCl_3$
KCl	KCl + $K_3NaMgCl_6$	$K_3NaMgCl_6$	$K_3NaMgCl_6$ + $KMgCl_3$	NaCl + $KMgCl_3$	Na_6MgCl_8 + $KMgCl_3$		Na_2MgCl_4 + $KMgCl_3$			$NaMgCl_3$

X-ray investigation of the DTA-samples confirm the new phases in addition to the known compounds (e.g. $0.5KCl+NaMgCl_3 \rightarrow 0.5KMgCl_3+0.5Na_2MgCl_4$) of the binary systems (ref.7). The diffractometer-diagram of $K_3NaMgCl_6$ (fig. 4) agrees well with the calculated intensities using the following parameters: space group $R\bar{3}c$ (No.167); a=12.01Å, c=13.87Å; K in e with x=-0.384, Na in a, Mg in b, Cl in f with x=-0.016 y=-0.178 z=0.097.

Thermodynamic Data by EMF-Measurements

In the range from 25 to 50 mole-% $NaMgCl_3$ on the section $KCl/NaMgCl_3$, three solid phases - $KMgCl_3$, $K_3NaMgCl_6$ and NaCl - coexist (abbreviated K_3Na). In a galvanic cell for solid electrolytes $(C+Cl_2)/KCl/K^+$-conducting glass$/K_3Na/(C+Cl_2)$, an e.m.f. (E) is generated by the 'cell-reaction'

$$2KCl+NaCl+KMgCl_3=K_3NaMgCl_6$$

From the relation $\Delta G_R=-n \cdot F \cdot E$ (n=transported K^+=2; F=Faraday constant) the free enthalpy of reaction can be calculated. Its temperature dependence can be assumed to be linear, so that the Gibbs-Helmholtz equation $\Delta G_R=\Delta H_R-\Delta S_R \cdot T$ directly yields the enthalpy and entropy of the reaction as temperature-independent quantities.

RESULT: At 665K and 613K the same e.m.f.=61±2mV was measured. This gives $\Delta G_R = \Delta H_R = -11.8 kJ \cdot mol^{-1}$, and $\Delta S_R = 0$.

Together with the free enthalpy for the reaction (ref.10)

$KCl + MgCl_2 = KMgCl_3 \quad \Delta G_R(kJ/mole) = -8.7 - 0.0167T$,

ΔG_R for the formation of $K_3NaMgCl_6$ from $3KCl + NaCl + MgCl_2$ can be calculated: $\Delta G_R(kJ/mole) = -21 - 0.0177T$ and $\underline{\Delta G_R(298K) = -26 kJ \cdot mol^{-1}}$, which gives $\Delta H_R = -21 kJ \cdot mol^{-1}$ and $\Delta S_R = +17 J \cdot K^{-1} \cdot mol^{-1}$.

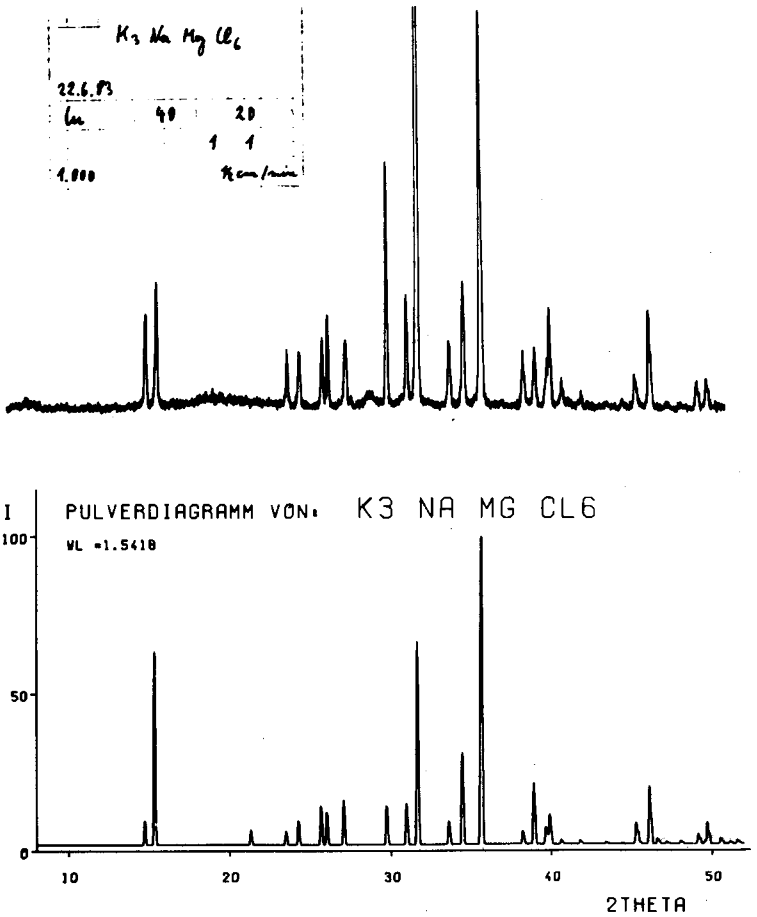

Fig. 4. Observed (above) and calculated X-ray intensities

There is the question of whether a mixture of the quaternary compound + KCl or K_4MgCl_6 + NaCl is stable at 20 mole-% $NaMgCl_3$. (ref.10)

$$4KCl + MgCl_2 = K_4MgCl_6 \qquad \Delta G_R(298K) = -20.7 kJ \cdot mol^{-1}$$

$$3KCl + NaCl + MgCl_2 = K_3NaMgCl_6 \qquad \Delta G_R(298K) = -26 kJ \cdot mol^{-1}$$

The subtraction of equation two from the first gives:

$$KCl + K_3NaMgCl_6 = K_4MgCl_6 + NaCl \qquad \underline{\underline{\Delta G_R(298K) = +5.3 kJ \cdot mol^{-1}}}$$

Because of the positive value of ΔG_R the phases ($K_3NaMgCl_6$+KCl) are stable at room temperature. This is confirmed by the X-ray investigations. Surprisingly for a cell KCl//22.5mole-% $NaMgCl_3$ a small e.m.f. of 2.0mV at 666K and 1.2mV at 611K was measured. This means that at higher temperatures a certain amount K_4MgCl_6 is stabilized by forming mixed-crystal with $K_3NaMgCl_6$.

Analogous compounds

Individual samples of $3KCl/NaCl/MCl_2$ (M=Fe, Mn, V, Cd) were investigated by DTA and X-ray. The temperatures of the peritectic and the lattice constants are listed in table 2. (*The vanadium compound is formed by a solid state reaction.)

Table 2.
Peritectic temperatures and lattice constants

	$T \cdot K^{-1}$	$a \cdot Å^{-1}$	$c \cdot Å^{-1}$
$K_3NaMgCl_6$	743	12.01	13.87
$K_3NaMnCl_6$	737	12.06	13.94
$K_3NaFeCl_6$	693	11.86 [3]	13.86 [3]
K_3NaVCl_6	860*	12.01	13.84
$K_3NaCdCl_6$	723	12.14	14.13

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