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THE PHASE DIAGRAM OF THE $AgNO_3$-KNO_3 SYSTEM DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

The phase diagram for the $AgNO_3$–KNO_3 system has been determined using differential scanning calorimetry (DSC). Eutectic point has been found at 391 K and X_{Ag} = 0.580 mole fraction $AgNO_3$. The DSC curves indicate the existence of an intermediate compound ($AgNO_3 \cdot KNO_3$) in the KNO_3-rich region of the phase diagram. This compound was identified in the solid phase by X-ray diffraction. The melting and the crystallization processes were followed with the aid of a hot stage microscope, too.

Keywords: $AgNO_3$–KNO_3 system, DSC, eutectic point, phase diagram

Introduction

Molten salt mixtures are in the field of interest of many investigations, owing to their application in chemical industry and energy storage systems. Phase diagrams give very valuable informations for predicting the possibility of their use in chemical technologies. However, in most cases the state diagrams available in the literature are old and often incomplete [1, 2]. Differential scanning calorimetry (DSC) gives reliable data on the chemical and phase equilibria of the studied system especially if combined with other methods, such as hot stage microscopy or X-ray diffraction measurements. In view of these facts, we wished to determine the phase diagram of the $AgNO_3$–KNO_3, bearing in mind that the last data measured in this binary system are dated back to the 1960's [1].

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Experimental

Reagent grade silver nitrate (Merck and Aldrich, 99.999%) and potassium nitrate (Merck) were used without any further purification, while potassium nitrate (Kemika, Zagreb) was recrystallized twice. Carefully dried and powdered salts were used for the preparation of the sample. Thermal measurements were carried out in the DSC cell of a DuPont 1090 TA system. The samples (about 20 mg) were weighed in an open golden pan. On the reference side an empty golden pan was used.The experiments were carried out in flowing air. No corrosion of the pan occurred during the heating and cooling cycles up to 623 K. A small reduction of silver nitrate to silver was visible, but its effect on the composition of the sample was negligible. The instrument was calibrated against indium (m.p. 429.7 K). The heating rate was 10 deg·min^{-1} while the cooling rate 5 deg·min^{-1}. Successive runs were repeated until well-pronounced peaks were obtained and the onset temperatures remained constant (usually in the second run). To achieve a direct correlation between a DSC peak and a phase transformation or chemical reaction in the sample, thermomicroscopic observations were carried out using a microscope, NU-2, Carl Zeiss, Jena, with a temperature programmed hot stage, for several compositions.

For the X-ray diffraction measurements a HZG-4/C, Carl Zeiss, Jena diffractometer was used. CoKα (λ = 0.179 nm) radiation and a Fe filter were employed. The speed of the goniometer was 1 deg·min^{-1}

The samples with the following compositions studied by X-ray diffraction: x_{Ag} = 0.670, 0.500, 0.273 and 0.020 (where x_{Ag} denotes the mole fraction of silver nitrate). The samples were melted and have been kept at 20 K above their melting point for 30 minutes then quenched to room temperature. This procedure was repeated three times. After solidifying, all the samples were powdered. The fine powder was used for X-ray phase analysis. The samples were investigated right after their preparation and a week later again.

Results and discussion

The phase diagram (Fig. 1) was established by cooling the melts, after they had been kept about 20 K above their melting point for 5 minutes. For the pure components very sharp exothermal peaks were observed. The onset temperatures during cooling were about 1 K below the onset temperatures observed in the heating process, which is probably due to supercooling effects. At the construction of the phase diagram these small supercooling effects were neglected and the onset temperatures for all transitions were used without any correction.

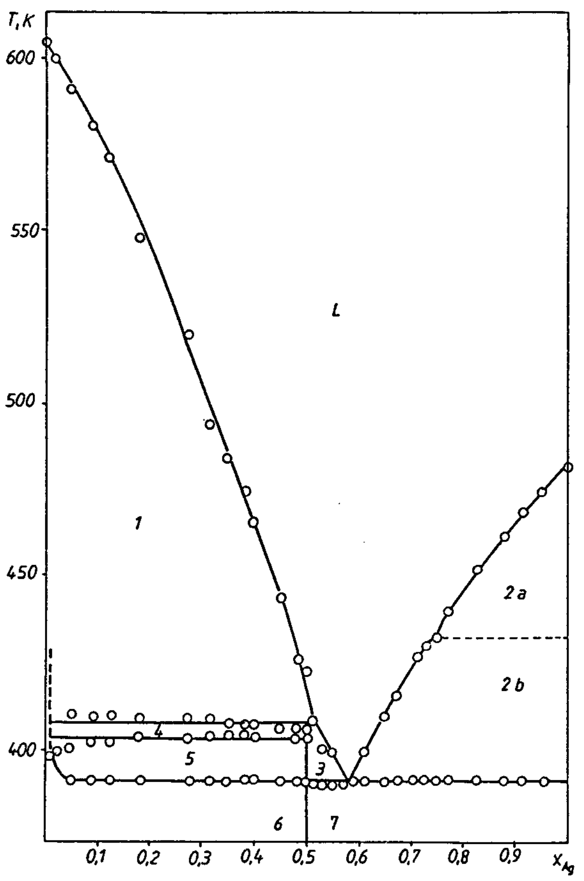

Fig. 1

Beside the melting or crystallization processes several phase transformations were observed in the pure components as well as in their mixtures.

First of all, there is an α → β transformation of KNO_3 that appears very reproducible at $T = 404$ K while heating the sample. The peak due to this transformation is visible in the binary systems when the mole fraction of KNO_3 is higher than 0.1. On cooling the reverse transformation is not complete. Two transformations are detected by the DSC: one at $T = 391$ K, the other at about $T = 353$ K.

Silver nitrate undergoes an α → β transformation on heating at $T = 432$ K, but usually only at the first run and only in the $AgNO_3$-rich region. A typical DSC cycle is presented in Fig. 2.

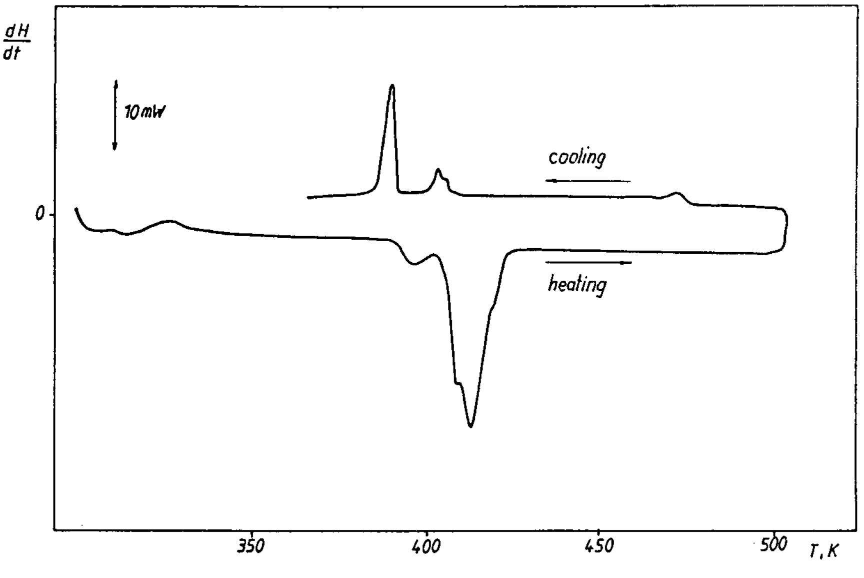

Fig. 2

In the samples with x_{Ag}<0.500 DSC peaks occur about 400 K, indicating a formation of an intermediate compound with an incongruent melting point. The peaks appear in a form of a doublet. With the increasing mole fraction of x_K (where x_K denotes the mole fraction of KNO_3) the doublet separates into two peaks (Fig. 3). The intensity of the peak at lower temperature is increasing with the mole fraction of the KNO_3. This peak probably corresponds to the $\beta \rightarrow \alpha$ transition of KNO_3.

The DSC peaks due to the compound formation are much smaller than it could be expected. The explanation of the small heat effect of this compound formation might be based on the fact that the true equilibrium can't be established during the heating and cooling cycles, and the formation of the intermediate compound is not complete. A peritectic point appears at x_{Ag} = 0.520 and T = 408 K, corresponding to the potential equilibrium of the melt, the compound and KNO_3.

Due to the non-equilibrium conditions, in region 4 and 5 the presence of some liquid was observed (confirmed by hot-stage microscopy). The border between region 5 and 6 (the lowest temperature peak in Fig. 3) corresponds to the solidification of this liquid and the phase transition of KNO_3. In spite of these conditions, we assume that Fig. 1 represents the equilibrium phase diagram.

The curvature on the solidus line suggests the existence of a solid solution at least over the range from x_K = 0.95 to x_K = 1.00. The explanation of the formation of a solid solution from silver nitrate and potassium nitrate or the intermediate compound is difficult, considering that the pure components crystallize in different space groups [3, 4]. However, the existence of different KNO_3 modifications [5] and the presence of other components in the melt may facilitate solid solution formation in a limited composition range. We have to add that the data for $x_K>0.95$ are uncertain to some extent.

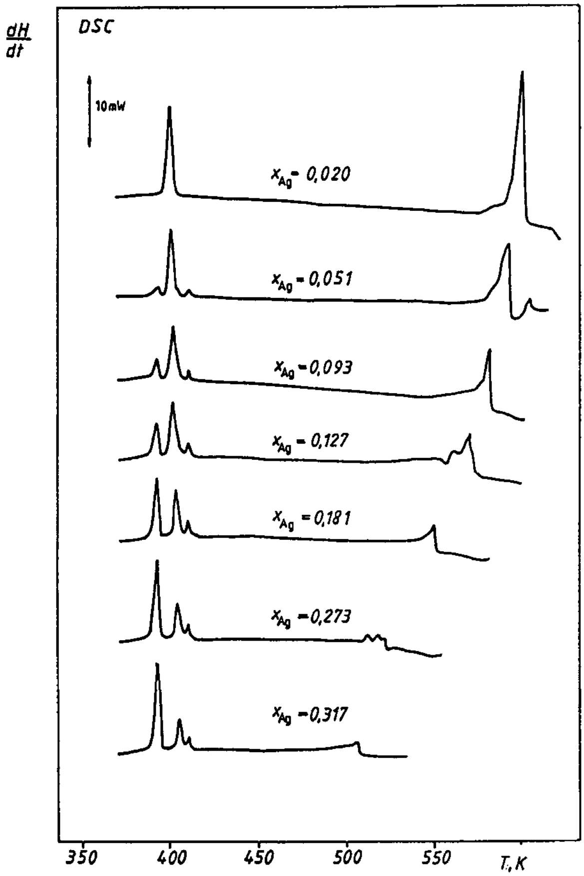

Fig. 3

The quasi-lattice structure of the molten components are different, too. The number of cations around the nitrate ion is six in the molten $AgNO_3$, while in the molten KNO_3 it is only three [6]. In the molten binary $AgNO_3$-KNO_3 system, where the ion mobility is greater, the existence of this compound is unlikely, although some exotherm interactions were detected by electrochemical measurements in this binary system [7].

Table 1 Onset temperatures at cooling in the system $AgNO_3$–KNO_3

x_{Ag}	Liquidus	Solidus	Other peaks	T/K
1.000	483	483	–	
0.954	474	391	–	
0.915	469	391	–	
0.882	462	391	–	
0.824	452	391	–	
0.769	439	391	–	
0.746	432	391	–	
0.730	430	391	–	
0.710	426	391	–	
0.670	416	391	–	
0.653	409	391	–	
0.609	400	390	–	
0.589	391	391	–	
0.566	390	390	–	
0.547	399	390	–	
0.529	400	390	–	
0.511	409	390	–	
0.499	423	390	–	
0.481	425	391	407*	
0.453	444	391	406*	
0.399	466	391	407*	
0.385	475	391	407*	
0.346	484	391	407*	
0.317	504	391	409*	
0.273	520	391	409	404**
0.181	548	391	409	404**
0.127	571	391	410	402**
0.093	580	391	409	402**
0.051	591	391	410	400**
0.020	599	399		
0.013	601	399		
0.009	602	398		
0.000	604	604	394	

*Doublets ($AgNO_3 \cdot KNO_3$ compound formation and probably a β → α transition of KNO_3 at $T \approx 404$ K)

** Peaks probably due to the β → α phase transformation of the KNO_3

A break on the liquidus line at $x_{Ag} = 0.73$ is due to the α → β phase transformation of $AgNO_3$. Namely, above $T = 433$ K only the β modification of $AgNO_3$ exists. The α → β phase transformation is kinetically controlled and during the DSC cycles the peak due to the α → β transition appears only at the first run. On the other hand, below $T = 433$ K only the α modification is stable.

All data from the cooling runs are presented in Table 1 and the corresponding phase diagram is shown in Fig. 1. The eutectic composition and temperature are $x_{Ag} = 0.580$ and $T = 391$ K, respectively. The circles on Fig. 1 represent the onset temperatures measured on cooling the samples of different compositions.

The X-ray measurements were performed to support the results of the DSC experiments. On the basis of the diffraction peaks, from the Bragg equation, the interplanar spacings (d) have been calculated. A compound formation was detected in all of the samples. The compound was identified as $AgNO_3 \cdot KNO_3$ in the solid phase by comparison the characteristic d values of the samples with the data of the ASTM cards [8]. The most characteristic peak of this compound appears even in the sample with very low mole fraction of $AgNO_3$ ($x_{Ag} = 0.020$).

For the sake of a better comparison of the diffractograms, they are presented together. Figure 4a shows the characteristic reflexions of the pure components and those of the sample with $x_{Ag} = 0.499$. As can be seen, beside the peaks of the $AgNO_3 \cdot KNO_3$ compound, the characteristic peaks of the pure components appear in the mixture as well, only with lower intensity. On Fig. 4b the diffractograms of the samples of different composition are presented. Beside the peaks of the pure components and the compound, several other peaks appear which do not belong to any possible decomposition product (Ag, Ag_2O) of these components. For the explanation of this phenomenon further investigations are needed.

The X-ray analysis was also carried out on samples with different mole fractions of $AgNO_3$ which had been crystallized from water, at different mole fraction of $AgNO_3$. Only the $AgNO_3 \cdot KNO_3$ compound was detected in these samples. However, the intensity of its characteristic peaks were lower, than of those crystallized from the melts.

The liquidus curve of the $AgNO_3$–KNO_3 system has been determined many times [1, 9]. There are small differences in the eutectic composition determined by different authors ($x_{Ag} \approx 0.38$), but as eutectic temperature $T_e = 404$ K is given by all the investigators. However, we have found an eutectic point at 0.580 mole fraction of silver nitrate and $T_e = 391$ K. The large difference in eutectic data between our results and the earlier ones is probably due to the different experimental techniques used for the determination of the phase diagram. The earlier investigators measured the heat effects on heating, worked with

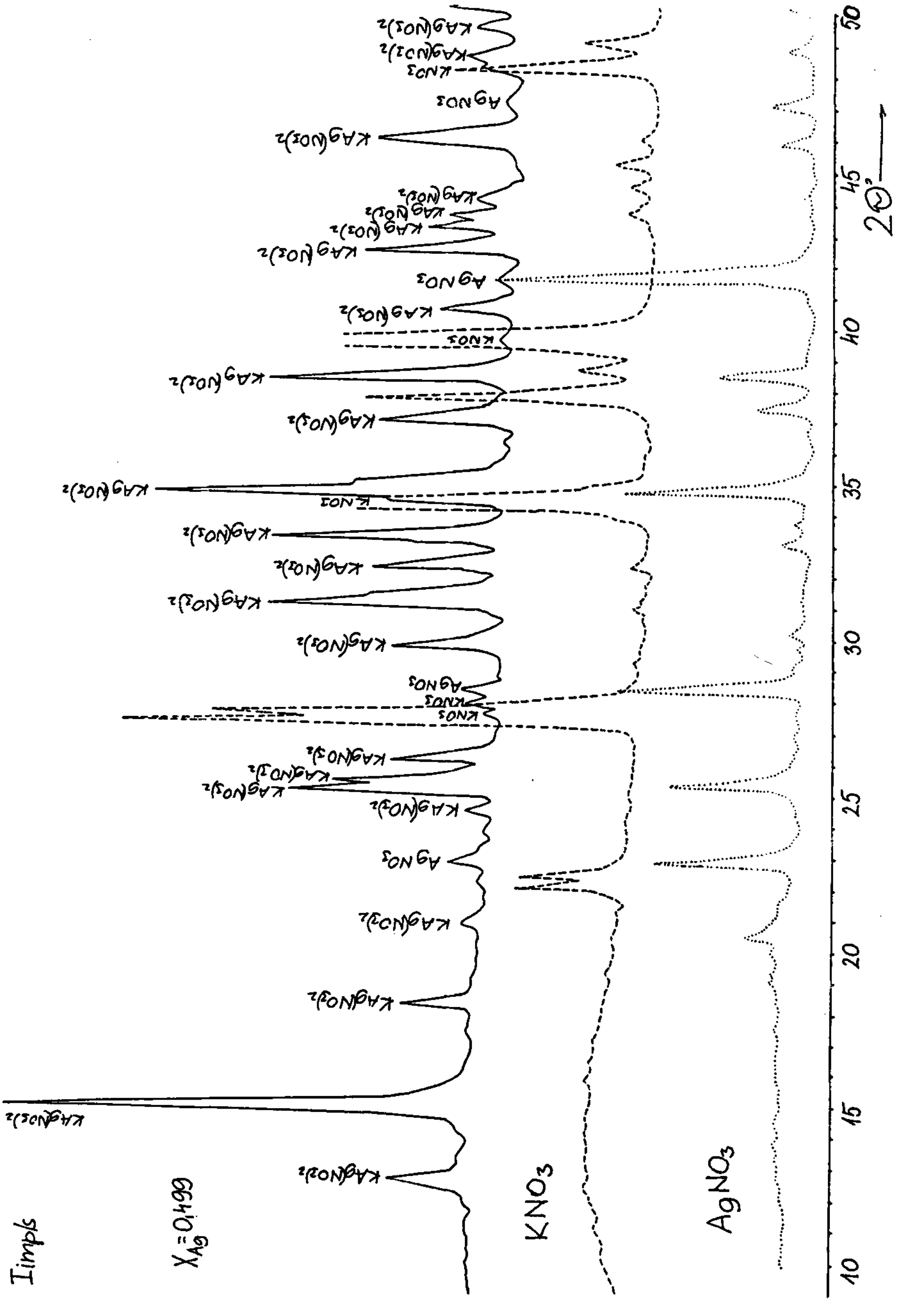
Imp/s
X_{Ag}=0.499
KNO$_3$
AgNO$_3$
KAg(NO$_3$)$_2$
AgNO$_3$
KNO$_3$
10
15
20
25
30
35
40
45
50
2Θ°

Fig. 4

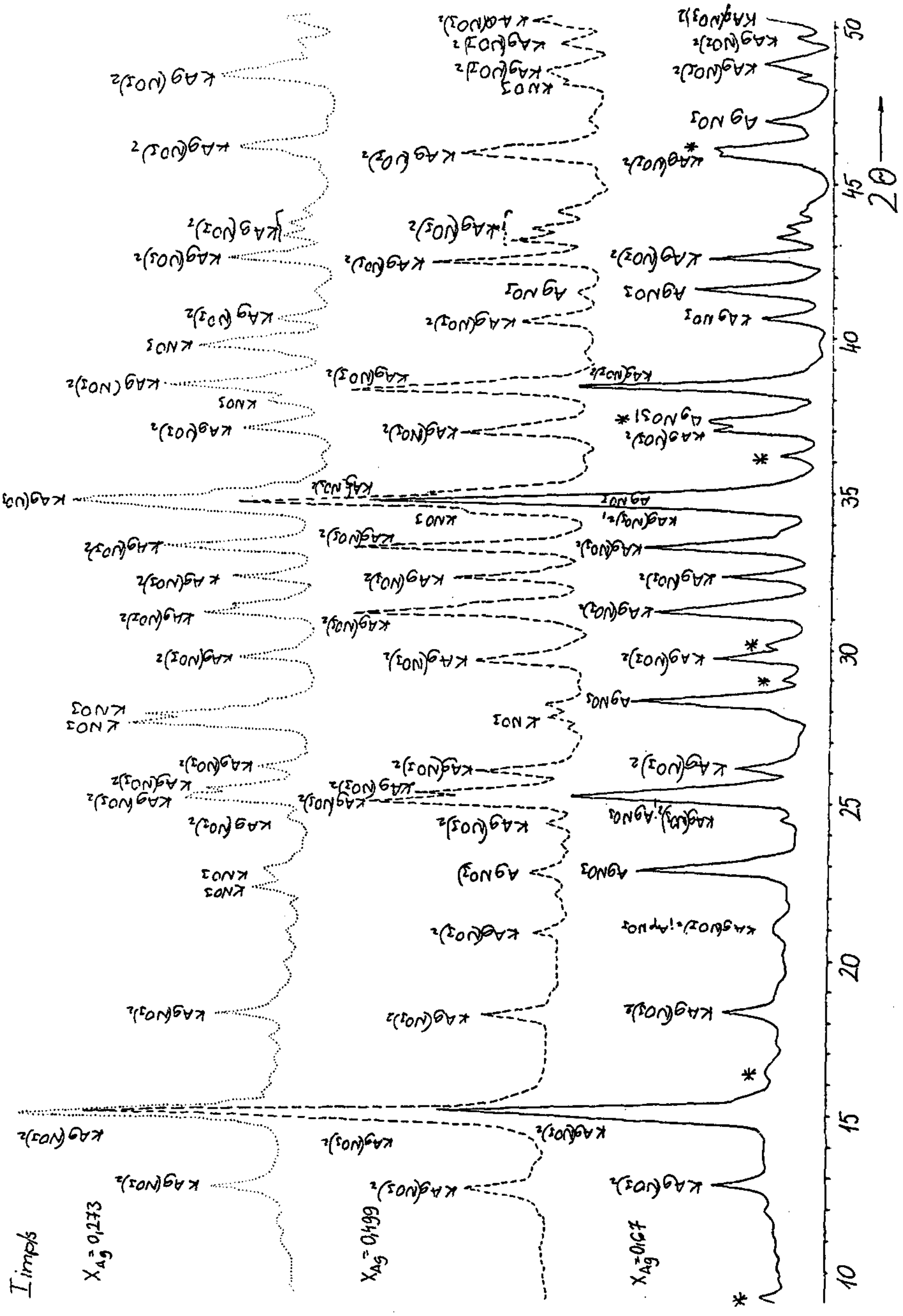
I imp/s
X_Ag = 0,273
X_Ag = 0,499
X_Ag = 0,167
KAg(NO3)2
KNO3
AgNO3
KAg(NO3)2, AgNO3
*
10
15
20
25
30
35
40
45
50
2θ

Fig. 5

large samples which were mechanically stirred. Under these conditions, on heating, it is difficult to separate the small heat effect due to the melting from the α → β transition of KNO_3. It can be assumed, that in the earlier studies the diagram was constructed on the basis of peak temperatures rather than onset values. As shown in Fig. 2, the differences between onset and peak temperatures are rather significant. On the contrary, by the DSC method, there is no problem in the detection of the small heat effect of the melting.

On cooling, at the eutectic temperature two processes take place, also: the transition of KNO_3 and the solidification of the sample. These processes were usually observed using the hot stage microscope.

In the $AgNO_3$-branch and the KNO_3-branch of the phase diagram there are no significant differences between our data and those determined by other methods.

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Zusammenfassung — Mittels DSC wurde das Phasendiagramm für $AgNO_3$–KNO_3 bestimmt. Bei 391 K wurde ein eutektischer Punkt mit einem Molenbruch von $x_{Ag} = 0.580$ gefunden. Die DSC-Kurve zeigt in der KNO_3-reichen Region des Phasendiagrammes die Existenz eines Zwischenproduktes ($AgNO_3KNO_3$) an. Diese Verbindung wurde im festen Aggregatzustand mittels Röntgendiffraktion identifiziert. Schmelz- und Kristallisationsprozesse wurden auch mit Hilfe eines Heiztischmikroskopes verfolgt.