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DTA ANALYSIS OF WATER EMANATION FROM THE SYSTEM $CuCl_2$ - KCl

K. Zurowski

INSTITUTE OF CHEMISTRY, HIGHER PEDAGOGICAL SCHOOL, 25-020 KIELCE, UL.
CHECINSKA 5, POLAND

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Mixtures of $CuCl_2$ and KCl in molar ratios of Cu to K of 0.5 to 2.0 were obtained at room temperature, and then subjected to DTA analysis in the temperature range 293–473 K. A number of endothermic effects were observed, the extents of these depending on the molar ratio of Cu to K in the mixture.

A DTA analysis of the system $CuCl_2$–KCl obtained at 473 K was earlier reported [1]. However, the phase changes in the system $CuCl_2$–KCl at high temperature, before and after the melting point, have not been described unambiguously. In the system $CuCl_2$–KCl at room temperature, $KCuCl_3 \cdot H_2O$ has been found [2]. $K_2CuCl_4 \cdot 2H_2O$ has also been described [3], which is converted into $KCuCl_3$ at 365-390 K [4]. At room temperature, independently of the molar ratio of Cu to K, $K_2CuCl_4 \cdot 2H_2O$ has been obtained by the evaporation of aqueous solutions [5].

The present work involved thermogravimetric investigations on the system $CuCl_2$–KCl, in which the molar ratio of Cu to K was varied from 0.5 to 2.0, within the temperature range 293–473 K.

Experimental

To obtain the system $CuCl_2$–KCl, dihydrous copper(II) chloride and potassium chloride (POCh, Gliwice) were used. Weighed quantities of the two salts were dissolved in distilled water and the solutions were next evaporated to dryness at 293 K during two weeks. The dry residue was crushed and ground. Mixtures with molar ratios of Cu to K of 0.5, 0.622,

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0.691, 0.768, 0.845, 0.922, 1.0, 1.2, 1.5 and 2.0 were prepared as described above.

Thermogravimetric analyses were performed with a derivatograph (MOM, Budapest, Hungary) within the temperature range 293-473 K. The measurement conditions were as follows: constant sample mass 1.200 g, corundum crucible, air atmosphere, Al_2O_3 as reference material, heating rate 1.25 deg/min, sensitivity DTA 1/5, sensitivity DTG 1/5, sensitivity TG 500 mg.

Results

Depending on the molar ratio of Cu to K in the investigated mixtures, the DTA curves demonstrate endothermic effects with peak temperatures of 336 K, 366 K, 388 K and 403 K. The curves reveal changes in the areas of the individual endothermic effects, or even their disappearance, as the molar ratio of $CuCl_2$ to KCl in the investigated samples is varied.

Figure 1 demonstrates that the area of the endothermic effect with peak at 336 K is the largest at a molar ratio of Cu to K of 1.0; on decrease of the ratio, the area gradually decreases to zero, while on increase of the ratio, the area gradually decreases not to zero.

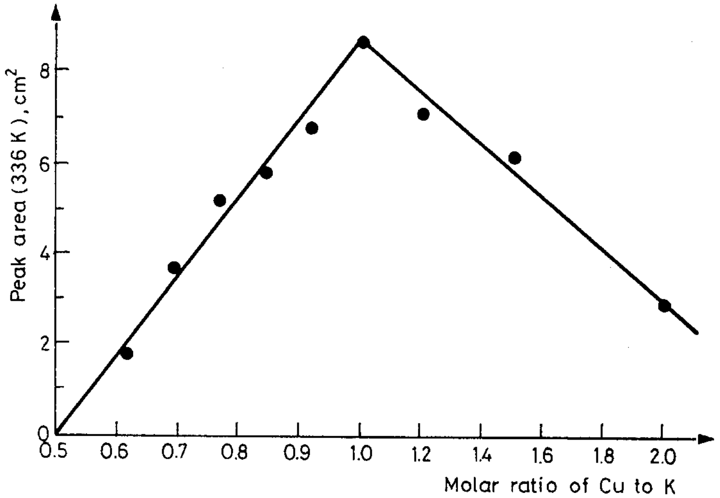

Fig. 1 Variation of the area of the endothermic effect with peak at 336 K as a function of the molar ratio of Cu to K in the mixture

Figure 2 demonstrates that the area of the endothermic effect with peak at 366 K is the largest at a molar ratio of Cu to K of 0.5; on increase of the ratio, the area gradually decreases to zero. The endothermic effect with peak at 366 K does not exist in the DTA curves of the mixtures with molar ratios of Cu to K higher than 1.0.

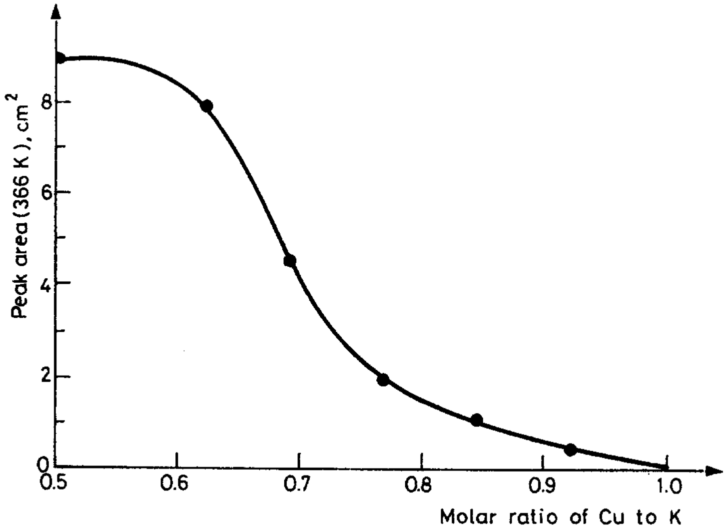

Fig. 2 Variation of the area of the endothermic effect with peak at 366 K as a function of the molar ratio of Cu to K in the mixture

Figure 3 demonstrates that the area of the endothermic effect with peak at 388 K is the largest at a molar ratio of Cu to K of 1.0; on increase or decrease of the ratio, the area gradually decreases, but not to zero. The area of the endothermic effect with peak at 403 K increases together with increase of the molar ratio of Cu to K above 1.0 (Fig. 4). The endothermic effect with peak at 403 K does not exist in the DTA curves of the mixtures with molar ratios Cu to K from 0.5 to 1.0. The mass loss of the samples under analysis takes place stepwise at 336, 366, 388 and 403 K, whereas it takes place continuously from 293 K up to the second endothermic peak at 366 K. When a very slow rate of heating was used during analysis (1.25 deg/min), the double character of the endothermic peak at 388 K was recorded.

Discussion

The endothermic effect with peak at 336 K is probably connected with regroupment of the elements in the crystal lattice of the investigated mixtures. The effects with peaks at 366 K and 388 K are connected with the dehydration of $K_2CuCl_4 \cdot 2H_2O$ described in [4], due to the reaction:

$$K_2CuCl_4 \cdot 2H_2O \rightarrow KCuCl_3 + KCl + 2H_2O \qquad (1)$$

The effect with peak at 403 K is connected with the known dehydration process of $CuCl_2 \cdot 2H_2O$ [6].

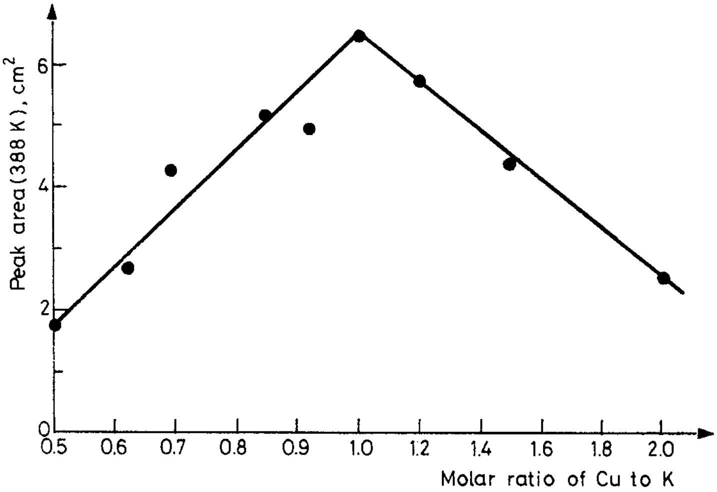

Fig. 3 Variation of the area of the endothermic effect with peak at 388 K as a function of the molar ratio of Cu to K in the mixture

The peak at 336 K does not exist in the DTA curves of the mixture with molar ratio of Cu to K equal to 0.5 and its area increases linearly (Fig. 1) until the molar ratio reaches a value of 1.0. In the same way, the $CuCl_2 \cdot 2H_2O$ contents in the mixtures increase above the stoichiometry of $K_2CuCl_4 \cdot 2H_2O$. It may be suggested that $CuCl_2 \cdot 2H_2O$ occupies the crystal lattice of $K_2CuCl_4 \cdot 2H_2O$ formed during crystallization of the mixtures [3]. The phase change at 336 K probably involves regroupment of the elements of $CuCl_2 \cdot 2H_2O$ inside the crystal lattice of $K_2CuCl_4 \cdot 2H_2O$. Water emanates from the mixtures, in a stepwise way at 336 K and continuously up to 366 K, as a result of this regroupment. The crystal lattice of $K_2CuCl_4 \cdot 2H_2O$ free of

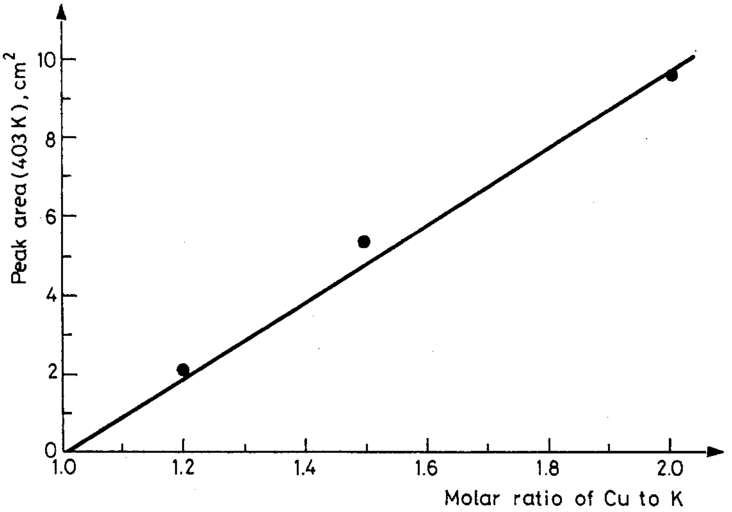

Fig. 4 Variation of the area of the endothermic effect with peak at 403 K as a function of the molar ratio of Cu to K in the mixture

$CuCl_2 \cdot 2H_2O$ undergoes a phase change at 366 K. Therefore, the area of the endothermic effect at 366 K decreases linearly to zero on inrease of the molar ratio of Cu to K in the mixtures from 0.5 to 1.0 (Fig. 2). In the mixtures with molar ratios of Cu to K equal to or higher than 1.0, $K_2CuCl_4 \cdot 2H_2O$ free of $CuCl_2 \cdot 2H_2O$ does not exist, and a phase change at 366 K was not observed. The phase change at 388 K exists in the DTA curve of the mixture with molar ratio of Cu to K equal to 0.5 (Fig. 3), due to reaction (1) [4]. The area of the peak at 388 K increases linearly on increase of the molar ratio of Cu to K from 0.5 to 1.0, as does the amount of $K_2CuCl_4 \cdot 2H_2O$ occupied by $CuCl_2 \cdot 2H_2O$ in the mixtures. Thus, the phase change at 388 K may also be attributed to the dehydration of the $K_2Cu_2Cl_6$ crystal lattice. At 388 K, probably two kinds of water emanate: that from $CuCl_2 \cdot 2H_2O$ and that from K_2CuCl_4, but also that from the $K_2Cu_2Cl_6$ crystal lattice (double character of the peak at 388 K). The areas of the peaks at 336 K and at 388 K decrease linearly on increase of the molar ratio of Cu to K in the mixtures to above 1.0. This seems obvious, since the amount of $K_2Cu_2Cl_6$ decreases in these mixtures. The phase change at 403 K is recorded only for the mixtures with molar ratios of Cu to K higher than 1.0, and the area of the peak at 403 K increases linearly (Fig. 4). This indicates the existence of a separate phase of $CuCl_2 \cdot 2H_2O$ in the mixtures, which loses water at 403 K [6].

Conclusions

Within the ranges of temperature and molar ratios studied here, mixtures of $CuCl_2$ and KCl exhibited endothermic processes at 336, 366, 388 and 403 K.

Three separate phases are formed in the mixtures of $CuCl_2$ and KCl during their crystallization at room temperature, i. e. $K_2CuCl_4 \cdot 2H_2O$, $(K_2CuCl_4 \cdot 2H_2O + CuCl_2 \cdot 2H_2O)$ and $CuCl_2 \cdot 2H_2O$. The amounts of these three phases depend on the molar ratio of Cu to K in the mixtures.

The $(K_2CuCl_4 \cdot 2H_2O + CuCl_2 \cdot 2H_2O)$ phase probably forms $K_2Cu_2Cl_6$ at 336 K, and partially loses the water up to 388 K.

The phase changes of the mixtures are connected with: regroupment of the $(K_2CuCl_4 \cdot 2H_2O + CuCl_2 \cdot 2H_2O)$ crystal lattice, reaction (1) of the $K_2CuCl_4 \cdot 2H_2O$ phase, emanation of water from the $K_2CuCl_4 \cdot 2H_2O$ and $K_2Cu_2Cl_6$ phases, and emanation of water from the $CuCl_2 \cdot 2H_2O$ phase.

In conclusion, it can be said that above 403 K there is no water in the investigated mixtures, and that the crystal lattice of $K_2Cu_2Cl_6$ is completely developed.

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Zusammenfassung — Bei Zimmertemperatur wurden Gemische aus $CuCl_2$ und KCl mit einem Cu:K Molverhältnis zwischen 0.5 und 2.0 erhalten und dann im Temperaturbereich 293-473 K einer DTA-Analyse unterzogen. Es konnte eine Anzahl von endothermen Effekten beobachtet werden, deren Größe eine Funktion des Cu:K Molverhältnisses im Gemisch ist.