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OBSERVATIONS ON THE SOLID SYSTEM $CuCl_2$-KCl IN THE TEMPERATURE RANGE 293-673 K

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The system $CuCl_2$-KCl was obtained at room temperature by evaporation of its aqueous solutions, and observations were made on its behaviour at room atmosphere and in an atmosphere poor in water. With the Boetius apparatus, mixtures of $CuCl_2$ and KCl were observed up to 673 K. The observations explain the unstable character of the solid system $CuCl_2$-KCl during its instrumental analysis in air atmosphere, and also explain the phenomenon of melting of the solid system $CuCl_2$-KCl with molar ratios of Cu to K of from 0.5 to 2.0. Conclusions were drawn on the constitution of the mixtures in the solid state, and also partially in the melt.

Keywords: solid system $CuCl_2$-KCl

Introduction

A mixture of $CuCl_2$ and KCl catalyses a very important ethylene oxychlorination process [1]. Even today, however, solid system $CuCl_2$-KCl and its liquid phase acting in the oxychlorination process have not been unequivocally clarified [2–4]. Direct instrumental investigations of the $CuCl_2$-KCl melt are very difficult as there are no standard data for the individual ions and the species in the mixtures at high temperature, and the melt has an unstable character. Further, the results of investigations on the solid phase $CuCl_2$-KCl are not clear-cut, because of its unstable character. For example, during X-ray investigations of the system $CuCl_2$-KCl, the green samples become brown, and then again turn green. To counteract this situation, it is necessary first of all to recognize the mechanism involved in the instability of the system. Fontana *et al.* [5] made assumptions concerning the state of aggregation of ionic and molecular species in the melt, and they did not expect the formation of solid solutions to alter the state of aggregation in the liquid phase.

The present work involved observations on the system $CuCl_2$-KCl at room temperature in air atmosphere and in an atmosphere poor in water, and also in the temperature range 293–673 K. The molar ratio of Cu to K in the samples was varied from 0.5 to 2.0.

The present investigations on the system $CuCl_2$-KCl, though simple as concerns the method, supplement the results presented in [6] and adequately explain the phenomenon of disappearance and growth of the peaks at 573–583 K and 603–618 K [7] in the DTA curves.

The samples were obtained by the evaporation of aqueous solutions of salts at room temperature, and also by their heating at 378 K (the temperature of obtaining an industrial catalyst of the type carrier-$CuCl_2$, KCl [8]).

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, in appropriate proportions, were dissolved in distilled water and the solutions were evaporated to dryness at 298 K, at room atmosphere for two weeks. The dry residue was crushed and ground. Some samples were next heated at 378 K for 12 h in air atmosphere. Two parts of the samples thus prepared were observed: at room temperature, and at room atmosphere in a desiccator over silica gel. The samples were also observed in the Boetius apparatus during heating up to 673 K at room atmosphere.

Results and discussion

Results

The observations on the samples at room temperature and room atmosphere are given in Table 1.

All samples of the investigated mixtures with molar ratios of Cu to K of from 0.5 to 1.0 are green after water evaporation at room temperature, while the mixtures with molar ratios of Cu to K of higher than 1.0 are greenish-blue. After a week in the room atmosphere, samples with molar ratios of Cu to K of from 0.622 to 1.0 become greenish-brown, and individual brown conglomerations are seen. The behaviour of the sample with a molar ratio of Cu to K of 0.5 is different: no brown conglomerations are seen in that sample. It becomes yellow-green after a

Table 1 Observations at room atmosphere on the system $CuCl_2$-KCl obtained at 293 K and at 378 K

Sample no.	Molar ratio Cu/K	Obtained at 293 K			Obtained at 378 K		
		Initial colour	After 1 week	After 2 weeks	Initial colour	After 1 day	After 2 weeks
1	0.5	green	green-yellow	green-yellow	brown	green-yellow	green-yellow
2	0.622	green	green-brown	green	brown	green	green
3	0.691	green	green-brown	green	brown	green	green
4	0.768	green	green-brown	green	brown	green	green
5	0.845	green	green-brown	green	brown	green	green
6	0.922	green	green-brown	green	brown	green	green
7	1.0	green	green-brown	green	brown	green	green
8	1.5	green-blue	green-blue	green-blue	brown	green-blue	green-blue
9	2.0	green-blue	green-blue	green-blue	brown	green-blue	green-blue

week. After two weeks, the initially obtained colours of samples with molar ratios of Cu to K of higher than 1.0 are stable. The yellowish-green colour of sample 1 is also stable. After two weeks, the samples with molar ratios of Cu to K of from 0.622 to 1.0 become green again. The samples heated at 378 K change their colour from brown to green after only one day, and they are then stable at room atmosphere even after two weeks. Depending on the molar ratio of Cu to K in the samples, the green colour varies. After one day, the brown colour of sample 1 changes to greenish-yellow, and that of samples 8 and 9 to greenish-blue. It was assumed that the changes in colour observed here result from the release and absorption of water. To support this assumption, all samples were placed in a desiccator, over silica gel. In the desiccator all the investigated samples except sample 1 changed from green to brown. The brown colour of samples obtained at 378 K is stable over silica gel in the desiccator.

The observations within the temperature range 293–673 K on samples obtained at 293 K are given in Table 2.

As seen in Table 2, the phase change occurs at 333–343 K. It takes place in the whole mass only for the mixture with a molar ratio of Cu to K of 1.0, and it does not take place in sample 1. Another (green) part of samples 1 and 4 undergoes the change at 363–403 K. Depending on the molar ratio of Cu to K in the mixtures, the melting point varies from 573–583 K (Cu to K = 0.5) to 603–623 K (Cu to K = 1.0 and 2.0). The melting process at 573–583 K does not take place in the whole mass of the mixture with a molar ratio of Cu to K of 0.768; the rest of the mixture melts at 603–623 K.

Small light crystals remain in the melt. The crystals slowly dissolve in the range 623–673 K.

Discussion

Mixtures of $CuCl_2$ and KCl with a molar ratio of from 0.5 to 1.0 become greenish-brown at room temperature and room atmosphere. In the samples with a molar ratio of Cu to K higher than 1.0, the brown colour may not be seen, due to the excess of the blue colour of $CuCl_2 \cdot 2H_2O$. This change in colour of the mixtures at room temperature has a reversible character. This may result from the release and absorption of water to or from the room atmosphere, depending on the air humidity. The ease of water release from mixtures with molar ratios of Cu to K higher than 0.5 may result from the existence and action of $CuCl_2 \cdot 2H_2O$ inside the crystal lattice of $K_2CuCl_4 \cdot 2H_2O$ (probably formed at room temperature [9]). Heating of the investigated mixtures at 378 K converts their colour to brown. This may result from the water release from mixtures according to the reaction:

$$K_2CuCl_4 \cdot 2H_2O \rightarrow KCuCl_3 + KCl + 2H_2O \text{ [9]} \qquad (1)$$

Table 2 Observations at 293–673 K on the $CuCl_2$ and KCl mixtures obtained at 293 K

Temp.	Sample no.			
section	1	4	7	9
to 333 K	green cryst.	green cryst.	green cryst.	green cryst.
333–343 K	green cryst.	crystals become brown, not in the whole mass	crystals become brown	crystals become brown, not in the whole mass
343–363 K	no change	green and brown crystals	brown cryst.	brown and green crystals
363–403 K	crystals become brown	crystals become brown	no change	crystals become brown
403–573 K	no change	no change	no change	no change
573–583 K	melting small crystals in the melt	partially melts	no change	no change
583–603 K	no change	no change	no change	no change
603–623 K	no change	full melt crystals in the melt	melting crystals in the melt	melting dark melt
623–673 K	crystals slowly dissolve	crystals slowly dissolve	crystals slowly dissolve	nothing is seen

At the same time, it may result from the water release from the crystal lattice of $K_2CuCl_4 \cdot 2H_2O$ occupied by $CuCl_2 \cdot 2H_2O$. Therefore, water may come from both combinations. All the above-mentioned changes have a reversible character, since after only one day the mixtures previously heated at 378 K become green at room atmosphere. The green-blue colour of the mixtures with molar ratios of Cu to K higher than 1.0 after only one day indicates that the crystal lattice of $CuCl_2 \cdot 2H_2O$ also loses water on heating of the mixtures, and next absorbs water from room atmosphere during the period of observation. The observations on the mixtures over silica gel in the desiccator at room temperature confirm that the observed changes in the mixtures at room temperature are connected with water exchange between the room atmosphere and the mixtures investigated here. The green colour of the samples in the desiccator changes to brown after only three days. The brown colour of the mixtures obtained at 378 K is stable even after two weeks in the desiccator.

The behaviour of samples formed at room temperature with molar ratios of Cu to K of from 0.622 to 2.0 differs from that of the sample with a molar ratio of 0.5. The change of the green colour of sample 1 to greenish-yellow may indicate the release of non-crystalline water from that mixture.

The observations made in the Boetius apparatus support the existence of three parts in the mass of the mixtures investigated here [6].

The first, which undergoes the phase change at 333–343 K, probably consists of the crystal lattice of $K_2CuCl_4 \cdot 2H_2O$ [9] together with the stoichiometric quantity of $CuCl_2 \cdot 2H_2O$ (1:1).

The second, the green one, which probably contains $K_2CuCl_4 \cdot 2H_2O$ (free of $CuCl_2 \cdot 2H_2O$), undergoes the phase change at 363–403 K [9].

The third part, which exists only in mixtures with molar ratios of Cu to K higher than 1.0, probably contains $CuCl_2 \cdot 2H_2O$.

The quantitative proportions of these three parts in the mixtures vary on change of the molar ratio of Cu to K in the mixtures.

Mixtures with molar ratios of Cu to K of 1.0 and higher melt at 603–623 K, whereas the mixture with a molar ratio of 0.5 melts at 573–583 K. Mixtures with molar ratios of Cu to K between 0.5 and 1.0 melt partially at 573–583 K, and the rest of their mass melts at 603–623 K.

Light crystals present inside the melt are probably KCl, which may result from reaction (1).

Conclusions

The solid-state mixtures of $CuCl_2$ and KCl obtained at room temperature exchange water with the atmosphere.

This water exchange has a reversible character depending on the atmospheric humidity.

All the water, i.e. crystalline and non-crystalline, is released from the investigated mixtures during their heating at 378 K.

The mixtures obtained at 378 K readily absorb water from the atmosphere.

The mixture with a molar ratio of Cu to K of 0.5 melts at 573–583 K. Mixtures with molar ratios equal to or higher than 1.0 melt at 603–623 K. Mixtures with molar ratios of Cu to K between 0.5 and 1.0 melt partially at 573–583 K and next at 603–623 K.

The existence of three parts in the mixtures of $CuCl_2$ and KCl obtained at room temperature is suggested here, i.e.
$K_2CuCl_4 \cdot 2H_2O$, $K_2CuCl_4 \cdot 2H_2O + CuCl_2 \cdot 2H_2O$ (1:1) and $CuCl_2 \cdot 2H_2O$,
depending on the molar ratio of Cu to K.

The last two conclusions explain the phenomenon of the disappearance and growth of the peaks in the DTA curves of the mixtures with molar ratios of Cu to K of from 0.5 to 1.0 [7].

There are light crystals in the melt of the mixtures investigated here, probably KCl, which dissolve near 673 K. The phase change at 673–693 K [7] may result from such dissolution.

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Zusammenfassung — Durch Verdampfen wäßriger Lösungen wurden bei Raumtemperatur $CuCl_2$ - KCl Systeme erhalten, deren Verhalten in normaler Raumatmosphäre und in wasserarmer Atmosphäre beobachtet wurde. Mittels eines Boetius Gerätes wurden Mischungen aus $CuCl_2$ und KCl bis zu einer Temperatur von 673 K beobachtet. Die Untersuchungen erklären den unstabilen Charakter des $CuCl_2$ – KCl Feststoffsystemes bei der instrumentellen Analyse in normaler Luftatmosphäre und erklären auch Die Erscheinung des Schmelzens des $CuCl_2$ – KCl Feststoffsystemes mit einem Cu zu K Molverhältnis von 0,5 zu 2,0. Es wurden Schlußfolgerungen über die Konstitution der Gemische im festen und teilweise auch im geschmolzenen Zustand gezogen.