OBSERVATIONS ON THE SOLID SYSTEM CuCl₂-KCl IN THE TEMPERATURE RANGE 293-673 K

K. Zurowski

INSTITUTE OF CHEMISTRY, PEDAGOGICAL UNIVERSITY, 25-020 KIELCE, UL. CHECİŃSKA 5, POLAND

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The system CuCl₂-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 CuCl₂ and KCl were observed up to 673 K. The observations explain the unstable character of the solid system CuCl₂-KCl during its instrumental analysis in air atmosphere, and also explain the phenomenon of melting of the solid system CuCl₂-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 CuCl₂-KCl

Introduction

A mixture of CuCl₂ and KCl catalyses a very important ethylene oxychlorination process [1]. Even today, however, solid system CuCl₂-KCl and its liquid phase acting in the oxychlorination process have not been unequivocally clarified [2-4]. Direct instrumental investigations of the CuCl₂-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 CuCl₂-KCl are not clear-cut, because of its unstable character. For example, during X-ray investigations of the system CuCl₂-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 CuCl₂-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 CuCl₂-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-CuCl₂, KCl [8]).

Experimental

To obtain the system CuCl₂-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