SOLUBILITY IN THE $K_2H_2P_2O_7$–$K_3HP_2O_7$–$K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O SYSTEM AT 0°C

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Received March 25th, 1982

The solubility in the $K_2H_2P_2O_7$–$K_3HP_2O_7$–$K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O system has been studied at 0°C. The results are discussed in terms of the possible application of the substances as components of multicomponent liquid fertilizers of the PK type.

At our Department, the K^+, $H^+ \parallel PO_4^{3-}$, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$–H_2O systems are studied systematically with regard to their possible application as constituents of multicomponent liquid fertilizers; the particular systems are thus chosen so as to comply with the requirement of pH in the range pH 5–9 and the temperature conditions of our climate zone. In the pseudoquinternary system of interest, $K_2H_2P_2O_7$–$K_3HP_2O_7$–$K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O, the ternary systems $K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O, $K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O, $K_2H_2P_2O_7$–$K_3H_2P_3O_{10}$–H_2O, $K_4HP_3O_{10}$–$K_3HP_2O_7$–H_2O, and $K_4HP_3O_{10}$–$K_2H_2P_2O_7$–H_2O have been investigated[1]. The four former ternary systems are boundary ones with respect to the complex system, the last ternary system constitutes its stable diagonal dividing it into two pseudoquaternary systems. The determined points of simultaneous crystallization of two solid phases at the edges and at the stable diagonal, however, are not sufficient to give a detailed insight into the crystallization regions across the entire systems. For this reason, the pseudoquinternary system has been studied as a whole in the present work.

EXPERIMENTAL

Chemicals

The potassium di- and triphosphates constituting the components of the system were prepared at our Department by the modified[2] procedures[3–6]. The starting substances for the preparations were K_2HPO_4, H_3PO_4, and KOH (all Lachema, Brno).

Study of the Phase Diagram

In the heterogeneous pseudoquinternary system under study, $K_2H_2P_2O_7$–$K_3HP_2O_7$–$K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O, all of the components except water contain phosphorus and

potassium, and moreover, in $K_2H_2P_2O_7$ and $K_3H_2P_3O_{10}$ their ratio is the same, *viz.* 1 : 1; so analytical data on their own are not sufficient to enable us to construct the solubility diagram. Therefore, this system has been studied, for the first time, by making use of the so-called balance approach[10], in which the solid phase is separated from the heterogeneous equilibrium mixture of known composition, weighed, and analyzed, and the liquid phase composition is determined as the balance. $K_2H_2P_2O_7.0{\cdot}5\ H_2O$, $K_3HP_2O_7.3\ H_2O$, $K_3H_2P_3O_{10}$, and $K_4HP_3O_{10}.H_2O$ were placed in polyethylene bottles in amounts such that the total weight of anhydrous phosphates was 2·5 g. Water was added in a quantity leaving part of the phosphates undissolved. The compositions of the phosphate mixtures covered the entire system in question, and they were chosen in sections with constant ratio of the two triphosphates or diphosphates. The equilibrium established within 5 weeks at the temperature of interest; no significant participation of hydrolysis was traced. After the equilibrium established, the contents of potassium and phosphorus in the liquid were determined, and the values (or those for the corresponding oxides) were plotted in the various sections in % K_2O–% P_2O_5 coordinates. By constructing the lines determined by these points, the two branches of the solubility curve and the position of the eutonic point in the section concerned were obtained.

The solid phase was rapidly sucked off and dried in air at room temperature for 24 h, within which the substance was well dried, yet dehydration of the crystallohydrates did not set in. After drying, the solid was weighed and analyzed for phosphorus and potassium. The composition of the solid phase was obtained as a result of this analysis, occasionally supplemented by chromatographic and X-ray diffraction measurements. The composition of the liquid phase then was expressed as the balance.

The system under study was depicted in a manner common for quaternary systems in which an exchange reaction takes place. By the stable diagonal $K_4HP_3O_{10}$–$K_2H_2P_2O_7$–H_2O the $K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–$K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system was divided into two quaternary systems: $K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–$K_2H_2P_2O_7$–H_2O and $K_4HP_3O_{10}$–$K_3HP_2O_7$–$K_2H_2P_2O_7$–H_2O. The results of the balance evaluation for the points on the eutonic curves were currently correlated with the eutonic curves in the % P_2O_5–% K_2O diagram.

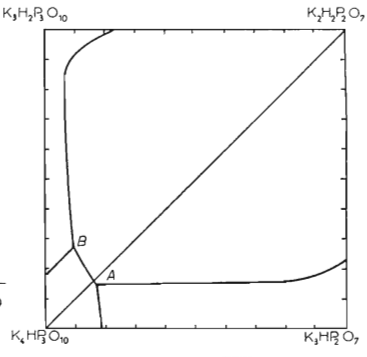

FIG. 1

Solubility diagram of the $K_2H_2P_2O_7$–$K_3HP_2O_7$–$K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O system at 0°C

Analytical Methods

Potassium was determined by atomic absorption spectrophotometry on a Varian Techtron 1200 instrument at 404·4 nm using an acetylene–air gas mixture. Phosphorus was analyzed spectrophotometrically by a modified procedure after Talvitie and coworkers[7]. Prior to the determination, the system was hydrolyzed by heating with approximately 2·5M-$HClO_4$ at 110°C for 3–5 h.

Other Methods

Thin layer chromatography was employed for a qualitative evaluation of the samples with respect to the possible effect of hydrolysis. Our procedure[8] was used applying the solvent system after Grunze and Thilo[9], up to now only used in paper chromatography. Use was also occasionally made of the X-ray diffraction method for the identification of the solid phase. The diffraction patterns were obtained on a Mikrometa 2 difffractograph (Chirana, Prague) using CuK_α radiation (power 35 kW, voltage 30 kV, current intensity 22 mA); the exposition period was 60–90 min.

TABLE I
Composition of the system

Composition of saturated solution, %		Composition of the solid phase	Composition of saturated solution, %		Composition of the solid phase
K_2O	P_2O_5		K_2O	P_2O_5	
31·5	34·9	$K_2H_2P_2O_7.0{\cdot}5\ H_2O$	30·6	36·4	$K_4HP_3O_{10}.H_2O$
31·6	32·2		30·5	37·0	
32·0	33·2		30·5	37·5	+
32·8	32·4	+	30·4	38·1	$K_3H_2P_3O_{10}$
33·1	32·5				
33·2	33·1	$K_3HP_2O_7.3\ H_2O$			
23·9	35·9	$K_2H_2P_2O_7.0{\cdot}5\ H_2O$	32·7	34·4	$K_4HP_3O_{10}.H_2O$
23·1	36·0		32·0	35·4	
22·9	36·5		31·6	36·2	+
24·8	37·4	+	31·1	36·9	
26·4	37·9		30·7	37·9	$K_2H_2P_2O_7.0{\cdot}5\ H_2O$
28·5	38·4				
29·7	38·6	$K_3H_2P_3O_{10}$			
36·5	37·5	$K_3HP_2O_7.3\ H_2O$			
36·2	35·6				
35·7	34·4				
35·1	33·3	+			
34·6	32·8				
33·6	32·9	$K_4HP_3O_{10}.H_2O$			

RESULTS AND DISCUSSION

For the first time the balance method[10] was used in a solubility study of a pseudoquinternary system. The method appeared to be sufficiently precise, the error due to the solid phase separation and drying being lower than that of the determination of potassium and phosphorus by the methods employed.

The curves of simultaneous crystallization of pairs of solids in the $K_2H_2P_2O_7$–$K_3HP_2O_7$–$K_3H_2P_3O_{10}$–$K_4HP_3O_{10}$–H_2O system are presented in square coordinates in Fig. 1. As the phase diagram demonstrates, there exist two points of simultaneous crystallization of three solids, labelled *A* and *B*. The composition corresponding to the point *A* is 33·3% K_2O and 33·9% P_2O_5; $K_3HP_2O_7$, $K_4HP_3O_{10}$, and $K_2H_2P_2O_7$, are in equilibrium. The composition of the point *B* is 30·4% K_2O and 38·8% P_2O_5; in equilibrium are $K_4HP_3O_{10}$, $K_3H_2P_3O_{10}$, and $K_2H_2P_2O_7$. The analytical data, in this case obtained directly along the curves of simultaneous crystallization of pairs of solids, are summarized in Table I.

The results of the study of the pseudoquinternary system are consistent with those concerning the solubility of potassium phosphates, obtained previously. The highest solubility is observed in mixtures from which triphosphate (particularly $K_4HP_3O_{10}$) crystallizes. This region is also virtually temperature-independent and the crystallization fields of the triphosphates are small as compared with those of the diphosphates.

From the point of view of a possible agrochemical application, the K_2O and P_2O_5 contents in the saturated solution and their ratio are of significance. The contents are highest in the points of simultaneous crystallization of three solids (points *A* and *B*) and on the line connecting them, and on the curve of simultaneous crystallization of $K_3HP_2O_7$ and $K_4HP_3O_{10}$. In the latter region the K/P ratio is also convenient, being greater than unity.

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Translated by P. Adámek.