SOLUBILITY IN THE KH_2PO_4–K_2HPO_4–$K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O SYSTEM AT 0°C

Miroslav EBERT, Ivan LUKEŠ, Jitka EYSSELTOVÁ, Jindřich NASSLER and Zdeněk MIČKA

Department of Inorganic Chemistry,
Charles University, 128 40 Prague 2

Received January 7th, 1983

The solubility was studied in the KH_2PO_4–K_2HPO_4–$K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system at 0°C. The results are discussed in terms of their application to the preparation of multicomponent PK type liquid fertilizers.

This work is part of our systematic study of the K^+, H^+ $\|$ PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$—H_2O system aimed at its utilization in multicomponent liquid fertilizers[1–3]. The partial systems therefore are chosen so as to comply with the requirements of pH lying in the range of 5–9 and temperature corresponding to our climate conditions. In the complex pseudoquinary KH_2PO_4–K_2HPO_4–$K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system, the KH_2PO_4–K_2HPO_4–H_2O system (as related to the K_3PO_4–H_3PO_4–H_2O system) was studied[4] at 25 and 0°C, and the $K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system was investigated[1] at 0°C. The two systems make up the edges of the pseudoquinary system in question. The two remaining edges are constituted by the KH_2PO_4–$K_2H_2P_2O_7$–H_2O and K_2HPO_4–$K_3HP_2O_7$–H_2O systems, the stable diagonal is formed by the KH_2PO_4–$K_3HP_2O_7$–H_2O system. These three systems were studied at temperatures of −7 or −8°C. The established points of simultaneous crystallization of two solid phases at the edges and the stable diagonal at various temperatures, however, fail to offer a sufficiently detailed insight into the crystallization regions over the entire system. Therefore, in this work the pseudoquinternary system is studied as a whole.

EXPERIMENTAL

Chemicals. KH_2PO_4 and K_2HPO_4 were commercial chemicals of reagent grade purity (Lachema, Brno), $K_2H_2P_2O_7.0{\cdot}5\ H_2O$ and $K_3HP_2O_7.3\ H_2O$ were our preparations synthesized by published procedures in our modification[5,6].

Study of the phase diagram. The solubility in the heterogeneous KH_2PO_4–K_2HPO_4–$K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system was studied by applying the balance approach[7] consisting in the separation and weighing of the solid from the mixture whose composition is known. Solid KH_2.

.PO_4, K_2HPO_4, $K_3HP_2O_7.3\ H_2O$, or KH_2PO_4, $K_2H_2P_2O_7.0{\cdot}5\ H_2O$, $K_3HP_2O_7.3\ H_2O$ in preselected quantities such that the total mass with respect to anhydrous phosphates was invariably 2·000 g, were placed in 80 polyethylene bottles, water was added in amounts leaving part of the phosphates undissolved, and the equilibrium was allowed to establish in 5 weeks during which the mixtures were occasionally stirred. By our experience, this period is long enough yet does not affect appreciably the phosphate distribution due to hydrolysis.

The samples were stored in a refrigerator where the temperature was held constant to within N2°C. The solubility of phosphates near 0°C is not very dependent on temperature[1,6]; at −2°C or +2°C the solubility changes by N0·1 to N0·3%. In view of the high concentrations of the solutions and with respect to the analytical methods employed, the precision of thermostatting can be regarded as sufficient.

After the equilibrium had been reached, the solid was collected on a pre-weighed glass filter and weighed. The weighing was repeated in 24 h after drying in air. In addition, samples of both the solid and the liquid were taken for analysis of the phosphorus and potassium contents. The values obtained were plotted, for the various sections, in % K_2O — % P_2O_5 coordinates. The two solubility curves were thus obtained; the point of their intersection represented the eutonic point. The contents of K_2O and P_2O_5 in the eutonic points established are given in Table I. The solid was dried, weighed, and analyzed for phosphorus and potassium. The composition of the solid phase was evaluated based on this analysis in conjugation with chromatographic and X-ray diffraction investigation and determination of diphosphate in the mixture with mono-

TABLE I

Composition of saturated solutions corresponding to the various solids systems

Composition		Composition	
% K_2O	% P_3O_5	% K_2O	% P_2O_5
$K_2PO_4 + K_2HPO_4.6\ H_2O$			
27·7	24·0	32·9	27·7
29·3	24·6	32·3	27·8
31·0	25·7	29·0	27·9
33·1	27·5		
$K_2HPO_4.6\ H_2O + K_3HP_2O_7.3\ H_2O$			
26·6	24·5	30·0	25·3
27·5	24·6	29·8	26·2
28·6	24·8	28·4	26·8
$KH_2PO_4 + K_2HPO_4.6\ H_2O + K_3HP_2O_7.3H_2O$			
28·1	27·9		
$KH_2PO_4 + K_3HP_2O_7.3\ H_2O$			
28·8	28·2	29·4	30·0
29·4	29·1	28·8	30·5

Composition		Composition	
% K_2O	% P_2O_5	% K_2O	% P_2O_5
$KH_2PO_4 + K_3HP_2O_7.3\ H_2O + K_2H_2P_2O_7.1/2\ H_2O$			
27·6	30·5		
$K_3HP_2O_7.3\ H_2O + K_2H_2P_2O_7.\frac{1}{2}\ H_2O$			
31·5	34·9	29·5	31·5
31·1	34·1	28·6	31·2
30·7	33·2	28·5	31·1
29·8	31·9		
$KH_2PO_4 + K_2H_2P_2O_7.\frac{1}{2}\ H_2O$			
17·5	26·8	24·1	28·6
19·0	26·9	26·0	29·7
21·2	27·3	26·3	30·3
23·4	28·6		

phosphate. The composition of the liquid phase then was obtained by calculation as the balance. The system under study was is portrayed in the conventional manner applied to quaternary systems in which an exchange reaction takes place. The KH_2PO_4-K_2HPO_4-$K_2H_2P_2O_7$--$K_3HP_2O_7$-H_2O system was divided by the KH_2PO_4-$K_3HP_2O_7$-H_2O stable diagonal into two quaternary systems, *viz.* KH_2PO_4-K_2HPO_4-$K_3HP_2O_7$-H_2O and KH_2PO_4-$K_2H_2P_2O_7$--$K_3HP_2O_7$-H_2O. The results of balance for the points on the eutonic curves were currently correlated with the eutonic curves in the % P_2O_5 — % K_2O diagram.

Analytical methods. Potassium was determined by atomic absorption spectrophotometry on a Varian Techtron 1 200 instrument at 404·4 mn using an acetylene–air gas mixture. Total phosphorus was determined spectrophotometrically by a modified procedure after Talvitie and coworkers^8. Prior to the analysis, the samples were hydrolyzed by heating with $HClO_4$ (approximately 2·5 mol l^{-1}) at 110°C for 3—5 h. In some points the diphosphate was determined in mixture with phosphate by a modified method after Jílek^9. The phosphate mixture was dissolved in water to a volume of about 70—100 ml, 5 g of NH_4Cl was added, and pH was adjusted to 4·2 with acetic acid. Zinc sulphate solution was added to separate $Zn_2P_2O_7$ as a precipitate, which was filtered our, washed with water acidified with acetic acid (pH 4·2), and dissolved in nitric acid; after pH adjustment the zinc was titrated with complexone.

Other methods. Thin layer chromatography was employed for a qualitative evaluation, particularly with respect to hydrolysis. Our procedure^{10} using a solvent system after Grunze and Thilo^{11} (before reserved for paper chromatography only) was applied. Occasionally, the solid phase was subjected to X-ray diffraction examination. The diffraction patterns were obtained on a Mikrometa 2 apparatus (Chirana, Prague) using $Cu_{K\alpha}$ radiation with a power of 35 kW, voltage 30 kV, intensity 22 mA. The exposition time was 60—90 min.

RESULTS AND DISCUSSION

The composition corresponding to the eutonic points for the KH_2PO_4-$K_2H_2P_2O_7$--H_2O and K_2HPO_4-$K_3HP_2O_7$-H_2O systems at 0°C approaches closely that establi-

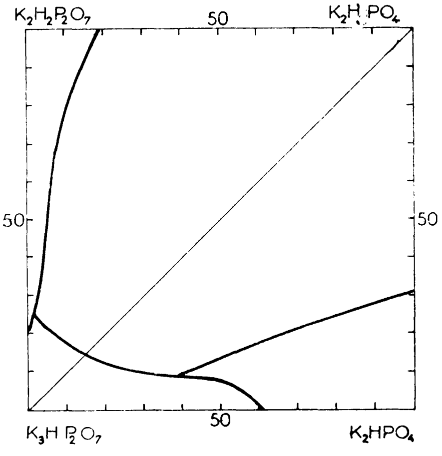

FIG. 1

Curves of simultaneous crystallization in the KH_2PO_4-K_2HPO_4-$K_2H_2P_2O_7$-$K_3HP_2O_7$--H_2O system at 0°C shed previously[5] at temperatures of -7 or -8°C. This is consistent with the slight dependence of polyphosphate solubility on temperature[1], particularly below 0°C.

The curves of simultaneous crystallization of two solids in the system under study, KH_2PO_4–K_2HPO_4–$K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O, are shown in Fig. 1. As follows from the phase diagram two points of simultaneous crystallization of three solids exist. The composition corresponding to one of them (point *A*) is 28·1% K_2O and 27·9% P_2P_5, the solids in equilibrium are KH_2PO_4, $K_2HPO_4.6\ H_2O$, and $K_3HP_2O_7.3\ H_2O$, the composition corresponding to the other point (point *B*) is 27·6% K_2O and 30·5% P_2O_5, and KH_2PO_4, $K_4HP_2O_7.3\ H_2O$, and $K_2H_2P_2O_7.0{\cdot}5\ H_2$ are in equilibrium. The analytical data, which in this case were derived directly along the curves of simultaneous crystallization of two solids, are summarized in Table I.

The results of this study of the pseudoquinternary system agree well with the data of phosphate solubilities obtained previously. The highest solubility is found on the edge representing the binary system of the two diphosphates, *i.e.* in the eutonic point of the $K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system. The solubility is lower if monophosphate is present.

From the point of view of the intended agrochemical application, the concentrations of K_2O and P_2O_5 in the saturated solution and their ratio are of importance. The content of the two oxides is highest in the above-mentioned eutonic point of the $K_2H_2P_2O_7$–$K_3HP_2O_7$–H_2O system, while the most favourable ratio of the concentrations, *viz.* $K/P = 1{\cdot}74$, is in the eutonic point of the K_2HPO_4–KH_2PO_4–H_2O system, this is the highest value found in the entire $K^+, H^+ \parallel PO_4^{3-}, P_2O_7^{4-}, P_3O_{10}^{5-}$–$H_2O$ system under study. The corresponding total content of the two oxides, however, is low, only amounting to 51·7%.

REFERENCES

1. Ebert M., Eysseltová J., Lukeš I., Nassler J.: This Journal *46*, 2633 (1981).
2. Ebert M., Lukeš I., Eysseltová J., Nassler J.: This Journal *48*, 1676 (1983).
3. Ebert M., Eysseltová J., Lukeš I., Nassler J.: Chem. Prům. *32/57*, 631 (1982).
4. Flatt R., Brunisholz G., Bourgeois J.: Helv. Chim. Acta 39, 841 (1956).
5. Nassler J., Sýbr M., Chrtianský L.: Unpublished results.
6. Ebert M., Eysseltová J., Lukeš I., Nassler J.: Chem. Prům. *30/55*, 516 (1980).
7. Eysseltová J., Kovářová B.: Chem. Zvesti, in press.
8. Talvitie N. A., Perez E., Illustre D. P.: Anal. Chem. *34*, 866 (1962).
9. Jílek A., Koťa J.: *Vážková analysa a elektroanalysa*, Vol. III. Published by SNTL, Prague 1956.
10. Ebert M., Lukeš I., Nassler J., Eysseltová J.: Chem. Prům. *30/55*, 402 (1980).
11. Grunze M., Thilo E.: *Die Papierchromatographie der kondensierten Phosphate*, p. 6. Akademie-Verlag, Berlin 1955.

Translated by P. Adámek.