

PSEUDO-TERNARY SECTIONS

IN $K_2H_2P_2O_7$ - $K_3HP_2O_7$ - $K_3H_2P_3O_{10}$ - $K_4HP_3O_{10}$ - H_2O SYSTEM

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Received December 22nd, 1980

Dedicated to Professor RNDr PhMr S. Škramovský on the occasion of his 80th birthday.

The solubility was studied in $K_2H_2P_2O_7$ - $K_3HP_2O_7$ - 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 , $K_3HP_2O_7$ - $K_4HP_3O_{10}$ - H_2O , and $K_4HP_3O_{10}$ - $K_2H_2P_2O_7$ - H_2O systems in the temperature region of +10 to -25°C. The results obtained are discussed with regard to the possible application of the systems as components in multicomponent PK type liquid fertilizers

As part of a systematic study of potassium phosphates, the solubility is investigated in multicomponent systems holding promise for agrochemical application. From this point of view, the desirable properties are high solubility not much temperature dependent, and the eutectic temperature below -20°C. Also, in agrochemistry it is aimed to achieve a K : P ratio exceeding unity in the mixture used.

At our department, the solubility is being studied in selected parts of the K^+ , $H^+ \parallel PO_4^{3-}$, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$ - H_2O system at temperatures below 0°C. The particular systems are chosen so that the pH lies in the region of 5-8. In the literature, the solubility has only been reported¹ for the K_2O - H_3PO_4 - $H_4P_2O_7$ - H_2O system at 25°C.

The salt composition of the complete K^+ , $H^+ \parallel PO_4^{3-}$, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$ - H_2O system can be represented by a trigonal prism, where the corners of one of the bases are the representative points of the acids concerned (H_3PO_4 , $H_4P_2O_7$, and $H_5P_3O_{10}$), those of the other base are the representative points of the respective salts with the maximum contents of potassium. The region covering the above-mentioned pH range is here determined by a set of sections representing the various systems involving two salts and water. Those systems whose representations are sections lying on the edge of the salt composition diagram are ternary ones. Systems represented by sections lying on the face of the diagram are pseudo-ternary if there exists such a saturated solution with which the two salts acting as the components are simultaneously in equilibrium. Obviously, systems suitable for a study will be such multicomponent systems as are bounded just by these ternary or pseudo-ternary systems. The pseudo-quintery $K_2H_2P_2O_7$ - $K_3HP_2O_7$ - $K_3H_2P_3O_{10}$ - $K_4HP_3O_{10}$ - H_2O system is a good example of such a choice.

EXPERIMENTAL

Chemicals

The potassium di- and triphosphates used as components in the system under study were original preparations synthesized by the modified² procedures reported in literature³⁻⁶. The starting chemicals for the preparations were KH_2PO_4 , H_3PO_4 , and KOH (allpur., Lachema, Brno).

Study of the Phase Diagrams

For attaining the desired temperatures, an Elektrosvit refrigerator, a Calex freezing box, and an MK 70 cryostat (Prüfgeräte-Werk Medingen, GDR) were used for the temperature regions of down to -5°C , -5 to -30°C , and below -30°C , respectively.

The solubility isotherms in the ternary systems were examined by the wet residue (Schreinemakers) method. Series of mixtures of the starting substances with different ratios of the components were placed in 50 ml vessels, water was added and the systems were equilibrated. During this process, the mixtures were recrystallized by repeated cooling. This lasted 3–4 weeks, during which, as checked chromatographically, the distribution of the various polyphosphates did not change. The establishment of the equilibrium was checked by spectrophotometric determination of the phosphorus content in the liquid phase. After the equilibrium established, the liquid phase and occasionally also the wet residue was analyzed. The liquid for analysis was sampled by means of a pre-cooled pipette, the wet residue was separated on a cooled glass filter.

The material sampled was analyzed for the phosphorus and potassium contents. In the $\text{K}_2\text{H}_2\text{P}_2\text{O}_7\text{-K}_3\text{H}_2\text{P}_3\text{O}_{10}\text{-H}_2\text{O}$ system the potassium/phosphorus ratio is $\text{K} : \text{P} = 1 : 1$, so that the knowledge of their contents alone was not sufficient for plotting the solubility curve. For this reason, the concentration of hydrogen ions was in addition also determined by pH-metric potentiometric titration; the precise knowledge of the original complex was also of assistance in the construction of the solubility diagram.

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 determined spectrophotometrically by using an adapted procedure after Talvitie and coworkers⁷. Prior to the determination, the system was hydrolyzed by heating with approximately $2.5 \text{ mol l}^{-1} \text{ HClO}_4$ to 110°C for 3–5 hours.

Other Methods

For a discussion of the possible effect of hydrolysis in the problem under study, the sample composition was checked qualitatively by using thin layer chromatography. The method modified by the authors⁸ was employed using the solvent system recommended by Grunze and Thilo⁹, before applied only to paper chromatography. X-ray diffraction was also occasionally used for identification of the solid phase.

RESULTS AND DISCUSSION

The $\text{K}_2\text{H}_2\text{P}_2\text{O}_7\text{-K}_3\text{HP}_2\text{O}_7\text{-K}_3\text{H}_2\text{P}_3\text{O}_{10}\text{-K}_4\text{HP}_3\text{O}_{10}\text{-H}_2\text{O}$ system is bounded by the $\text{K}_2\text{H}_2\text{P}_2\text{O}_7\text{-K}_3\text{HP}_2\text{O}_7\text{-H}_2\text{O}$ and $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10}\text{-K}_4\text{HP}_3\text{O}_{10}\text{-H}_2\text{O}$ ternary systems and

TABLE I

Solubility in the $K_2H_2P_2O_7-K_3HP_2O_7-H_2O$ system

Composition of the liquid phase, %			Solid phase
$K_3HP_2O_7$	$K_2H_2P_2O_7$	H_2O	
$t = -10^\circ C$			
35.2	21.4	43.4	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
38.9	18.2	42.9	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
45.5	13.1	41.4	$K_2H_2P_2O_7 \cdot 0.5 H_2O + K_3HP_2O_7 \cdot 3 H_2O$
50.3	6.24	43.5	$K_3HP_2O_7 \cdot 3 H_2O$
$t = -15^\circ C$			
36.5	21.4	42.1	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
39.8	16.0	44.2	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
44.5	12.2	43.3	$K_2H_2P_2O_7 \cdot 0.5 H_2O + K_3HP_2O_7 \cdot 3 H_2O$
47.2	7.35	45.5	$K_3HP_2O_7 \cdot 3 H_2O$

TABLE II

Solubility in the $K_3H_2P_3O_{10}-K_4HP_3O_{10}-H_2O$ system

Composition of the liquid phase, %			Solid phase
$K_4HP_3O_{10}$	$K_3H_2P_3O_{10}$	H_2O	
$t = +10^\circ C$			
0.0	60.5	39.5	$K_3H_2P_3O_{10}$
31.8	34.1	34.1	$K_3H_2P_3O_{10}$
47.7	22.0	30.3	$K_3H_2P_3O_{10}$
58.5	6.93	34.6	$K_4HP_3O_{10} \cdot H_2O$
$t = -10^\circ C$			
0.0	57.2	42.8	$K_3H_2P_3O_{10}$
43.4	22.7	33.9	$K_3H_2P_3O_{10}$
57.5	11.6	30.9	$K_4HP_3O_{10} \cdot H_2O$
58.4	6.82	34.8	$K_4HP_3O_{10} \cdot H_2O$

the $K_2H_2P_2O_7-K_3H_2P_3O_{10}-H_2O$ and $K_3HP_2O_7-K_4HP_3O_{10}-H_2O$ pseudo-ternary systems. The $K_4HP_3O_{10}-K_2H_2P_2O_7-H_2O$ diagonal appeared to be the stable one.

The solubility data of the systems under investigation are summarized in Tables

TABLE III

Solubility in the $K_4HP_3O_{10}-K_3HP_2O_7-H_2O$ system at $-18^\circ C$

Composition of the liquid phase, %			Solid phase
$K_4HP_3O_{10}$	$K_3HP_2O_7$	H_2O	
64.8	0	35.2	$K_4HP_3O_{10} \cdot H_2O$
63.5	4.1	32.4	
62.8	10.2	27.0	
54.3	17.8	27.9	$K_3HP_2O_7 \cdot 3 H_2O$
35.2	28.9	35.9	
12.1	41.3	46.6	
0	46.9	53.1	$K_3HP_2O_7 \cdot 3 H_2O + ice$

TABLE IV

Solubility in the $K_4HP_3O_{10}-K_2H_2P_2O_7-H_2O$ system

Temperature $^\circ C$	Composition of the liquid phase, %			Solid phase
	$K_2H_2P_2O_7$	$K_4HP_3O_{10}$	H_2O	
+10	48.3	0	51.7	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
0	46.7	0	53.3	
-10	43.0	0	57.0	
+10	35.2	12.9	51.9	
0	38.4	13.1	48.5	
-10	41.1	10.0	48.9	
0, +10	26.2	32.9	40.9	
-10, -15	22.9	33.4	43.7	
+10	24.2	33.2	42.6	
+10 to -15	26.8	33.5	39.7	
+10 to -15	20.8	41.7	37.5	
+10 to -20	16.9	47.2	35.9	
-25	12.2	59.3	28.5	
+10 to -25	6.0	61.5	32.5	$K_2H_2P_2O_7 \cdot 0.5 H_2O +$ $+ K_4HP_3O_{10} \cdot H_2O$
+10 to -25	0	63.5	36.5	

I–V. The $K_2H_2P_2O_7-K_3HP_2O_7-H_2O$ and $K_3H_2P_3O_{10}-K_4HP_3O_{10}-H_2O$ systems were treated as parts of the $K_2H_2P_2O_7-K_4P_2O_7-H_2O$ and $K_3H_2P_3O_{10}-K_5P_3O_{10}-H_2O$ systems, respectively. The solubility diagrams of these systems are shown in

TABLE V
Solubility in the $K_3H_2P_3O_{10}-K_2H_2P_2O_7-H_2O$ system

Composition of the liquid phase, %			Solid phase
$K_3H_2P_3O_{10}$	$K_2H_2P_2O_7$	H_2O	
$t = +10^\circ C$			
0	48.3	51.7	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
21.1	31.7	47.2	
26.0	27.9	46.1	
32.2	24.1	43.7	
45.0	17.1	37.9	
52.2	7.5	40.3	$K_3H_2P_3O_{10}$
61.0	0	39.0	
$t = -5^\circ C$			
0	45.1	54.9	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
11.0	37.3	51.7	
19.2	31.8	49.0	
23.2	29.7	47.1	
33.7	21.1	45.2	
47.6	15.8	36.6	$K_3H_2P_3O_{10}$
50.3	11.2	38.5	
59.3	0	40.7	
$t = -10^\circ C$			
0	42.0	58.0	$K_2H_2P_2O_7 \cdot 0.5 H_2O + \text{ice}$
9.1	33.8	57.1	
20.0	29.8	50.2	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
35.1	20.5	44.4	
42.4	18.1	39.5	
49.2	11.8	39.0	$K_3H_2P_3O_{10}$
57.2	0	42.8	
$t < -15^\circ C$			
43.8	15.3	40.9	$K_2H_2P_2O_7 \cdot 0.5 H_2O$
48.3	11.9	39.8	$K_3H_2P_3O_{10}$
57.2	0	42.8	

Figs. 1 and 2. In the case of the $K_2H_2P_2O_7-K_4P_2O_7-H_2O$ system, our results can be compared with those obtained by Frazier and coworkers¹ at 0°C and 25°C. A satisfactory agreement was found for the data at 0°C. The $K_5P_3O_{10}-K_3H_2P_3O_{10}-H_2O$ system has not been investigated before in this manner, and our study resulted in the discovery of tetrapotassium hydrogentriphosphate, $K_4HP_3O_{10} \cdot H_2O$.

TABLE VI

Composition in the points of simultaneous crystallization of two solids. Hydration is disregarded for simplicity

Coexisting solids	K ₂ O %	P ₂ O ₅ %	K/P	Temperature °C
$K_3HP_2O_7 + K_4HP_3O_{10}$	34.6	36.9	1.41	-18
$K_4HP_3O_{10} + K_2H_2P_2O_7$	31.7	37.6	1.27	below -10
$K_4HP_3O_{10} + K_3H_2P_3O_{10}$	30.0	36.4	1.24	-15
$K_2H_2P_2O_7 + K_3H_2P_3O_{10}$	22.5	33.9	1.00	-15
$K_3HP_2O_7 + K_2H_2P_2O_7$	26.0	28.5	1.37	-15
$K_3HP_2O_7 + K_2H_2P_2O_7^a$	28.3	32.7	1.30	-18
$K_2H_2P_2O_7 + K_3H_2P_3O_{10}^a$	25.4	34.6	1.00	-18

^a Points of the unstable diagonal.

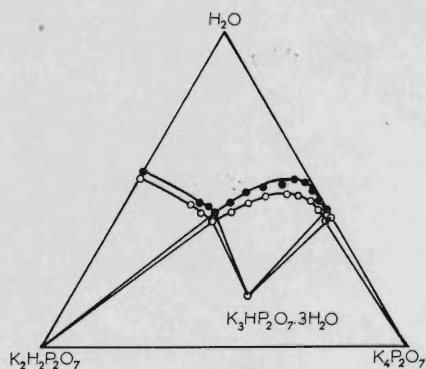


FIG. 1

Solubility in the $K_2H_2P_2O_7-K_4P_2O_7-H_2O$ system. Temperature: ● -15°C, ○ -10°C

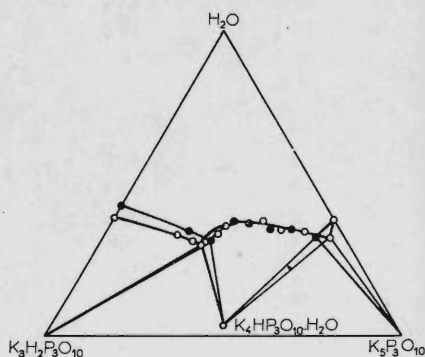


FIG. 2

Solubility in the $K_3H_2P_3O_{10}-K_5P_3O_{10}-H_2O$ system. Temperature: ● -10 to -25°C, ○ 10°C

As a common characteristics of all of the systems studied, their phases are highly soluble, the solubility being only slightly temperature dependent. Moreover, the results indicate that the temperature dependence in the pH region applied diminishes with increasing anion size, and ultimately the solubility of triphosphates is virtually temperature independent over a wide temperature region.

In all the systems, the solubility is highest in the points of simultaneous crystallization of two solid phases. The composition of these solutions is given in Table VI, where the points of simultaneous crystallization of two solids on the unstable $K_3H_2P_3O_{10}-K_3HP_2O_7-H_2O$ diagonal are shown as well.

As follows from Table VI, the presence of triphosphates, particularly $K_4HP_3O_{10} \cdot H_2O$, improves appreciably most of the agrochemically significant characteristics of the systems under study.

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Translated by P. Adámek.