Researches Of The Solubility Of Copper Sulfate In Orthophosphoric Acid At 30 And 80°C

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Abstract: With introduction of trace elements in the composition of phosphate-containing fertilizers, the formation of various compounds of trace elements with different solubility, depending on the place of introduction. The article presents the results of a study of the copper sulfate-phosphoric acid-water system at 30 and 80°C. The solubility diagram of the $CuSO_4$-H_3PO_4-H_2O system at 30°C has one branch corresponding to the release of $CuSO_4 \cdot 5H_2O$ copper sulphate pentahydrate into the equilibrium solid phase, and the solubility isotherm of the system at 80°C consists of two branches: the first branch the solubility curve corresponds to saturated solutions, of which copper sulfate pentahydrate crystallizes into the solid phase, the second branch corresponds to the formation of a new compound $CuSO_4 \cdot CuHPO_4 \cdot 2H_2O$ in the system.

Index Terms: phosphoric acid, copper sulfate, viscosity, density, copper, monocalcium phosphate, trace elements, sulfates, mineral fertilizers, micronutrients, copper phosphates.

1. INTRODUCTION

The problem of using micronutrients in agriculture is an important part of the theory and practice of mineral nutrition of plants. The science-based use of micronutrient fertilizers allows not only to increase the yield of agricultural crops, but also to produce food and feed balanced in composition [1]. Microelements due to their catalytic action allow plants to more effectively use the basic nutrients - solar energy, water and macrocells - nitrogen (N), phosphorus (P) and potassium (K), which in turn positively affects plant productivity and crop quality. Researches of the interaction of trace elements with components of mineral fertilizers are of great interest. In connection with this, many researchers conduct various experiments, set up experiments, and try to recreate the processes of the formation of trace elements. From this point of view, it is necessary to justify the theoretical foundations of the interaction of trace elements with acids, bases and salts. Thermodynamic studies of the interaction of sulfate salts of trace elements with phosphoric acid showed that when copper sulfate is introduced into phosphoric acid at 25°C, no interaction occurs and the trace elements are in solution in the form of sulfates, and in the presence of monocalcium phosphate, one or two substituted metal phosphates can form [2 -four]. However, it is known from the literature that, with increasing temperature of the solution, trace element sulfates change their hydration and solubility, and monocalcium phosphate undergoes hydrolysis with the release of phosphoric acid [5-6].

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2 METHODS OF RESEARCH

Therefore, it was interesting to find out in what form copper sulfate is found under conditions of obtaining double superphosphate, what is its solubility in phosphoric acid, how microelements behave in the presence of monocalcium phosphate. To this end, we studied the systems of copper sulfate - phosphoric acid - water and the interaction of sulfate salts of copper, zinc and cobalt with monocalcium phosphate at 30 and 80 ° C. The copper sulfate – phosphoric acid – water system at 30 and 80 ° C was studied by us by the isothermal solubility method. The solubility diagram of the system at 30 ° C has one branch, corresponding to the precipitation of copper sulfate pentahydrate into the equilibrium solid phase (Table 1, Fig. 1.)

Table 1. *Solubility data in the $CuSO_4$-H_3PO_4-H_2O system at 30 ° C*

comp	Composition of the liquid phase, mass,%		Composition of the solid "residue" mass,%		D, g/cm^3	μ, cct	Solid phase
	P_2O_5	$CuSO_4$	P_2O_5	$CuSO_4$			
	0,00	20,00					$CuSO_4 \cdot 5H_2O$
1.	5,61	16,87	0,75	57,24	1,2704		also
2.	9,55	14,60	1,32	55,39	1,2837		-"-
3.	14,29	12,36	3,62	50,42	1,3139	2,9790	-"-
4.	18,51	10,53	6,35	46,03			-"-
5.	24,40	8,89	8,22	44,85	1,3647	3,6840	-"-
6.	28,92	8,18	8,38	47,84	1,4097	3,8910	-"-
7.	31,40	7,79	8,12	49,20	1,4248	4,3571	-"-
8.	34,70	7,77	7,75	51,00	1,4598	4,9108	-"-
9.	37,99	7,77	10,09	48 ,53		5,7003	-"-

10.	42,60	7,77	9,07	52,18	1,5598	8,0986	-"-
11.	60,05	7,77	18,51	46,50			-"-

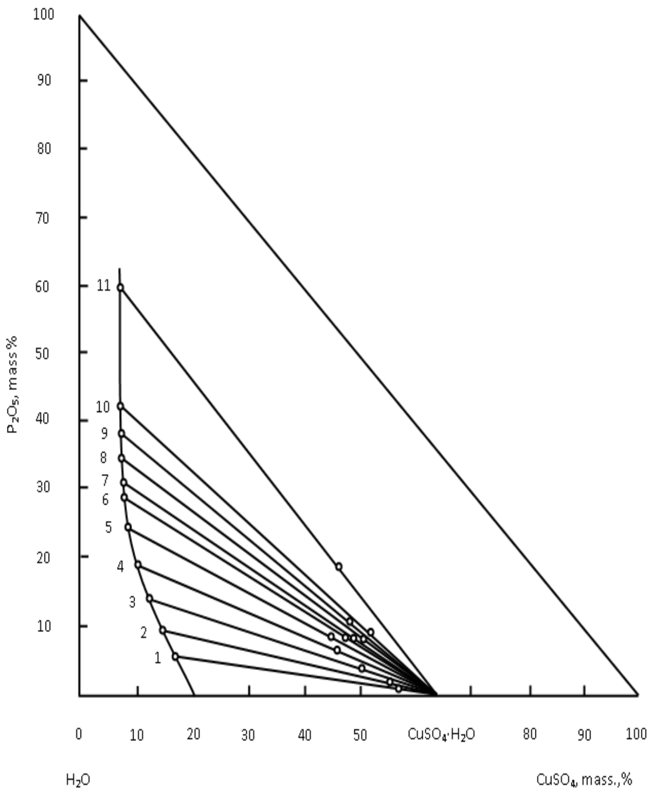

Fig. 1. *The solubility isotherm of the $CuSO_4$-H_3PO_4-H_2O system at 30 ° C*

When phosphoric acid is added to saturated copper sulfate solutions, the solubility of the latter decreases from 20.00 mass% to 7.77 mass%. When the concentration of phosphoric acid is equal to 31.40% and higher in phosphoric anhydride, the solubility of copper sulfate remains constant. Study of the viscosity and density of saturated solutions in the system of copper sulfate — phosphoric acid — water at 30 ° C shows that with an increase in the concentration of phosphoric acid, the above properties of solutions increase (Fig. 2, 3). The solubility isotherm of the $CuSO_4$-H_3PO_4-H_2O system at 80 ° C consists of two branches (Table 2, Fig. 4.).

Table 2. *Solubility data in the $CuSO_4$-H_3PO_4-H_2O system at 80 ° C*

comp po	Composition of the liquid phase, mass %		Composition of the solid "residue" mass%		Solid phase
	P_2O_5	$CuSO_4$	P_2O_5	$CuSO_4$	
	0,00	34,94			$CuSO_4 \cdot 5H_2O$
1.	2,10	34,01	0,25	57,51	also
2.	5,86	32,13	1,47	55,63	-"-
3.	12,33	29,15	1,23	58,88	-"-
4.	17,86	26,44	2,70	56,89	-"-
5.	23,63	24,13	4,73	56,10	-"-
6.	30,42	20,38	4,53	64,05	$CuSO_4 \cdot 5H_2O$ + $CuSO_4 \cdot CuHPO_4 \cdot 2H_2O$
7.	30,60	17,03	24,51	58,32	$CuSO_4 \cdot CuHPO_4 \cdot 2H_2O$
8.	32,69	13,44	23,64	69,21	also
9.	37,62	10,41	23,31	61,47	-"-
10.	46,20	6,89	23,63	62,84	-"-
11.	50,35	5,88	24,65	57,37	-"-

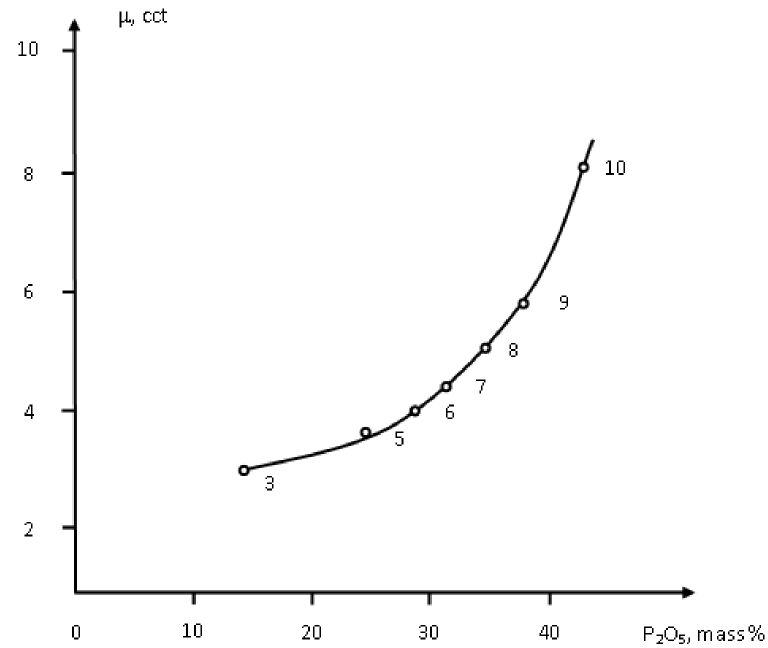

Fig. 2. *The change in the viscosity of saturated solutions in* $CuSO_4$-H3PO$_4$-H2O at 30 ° C

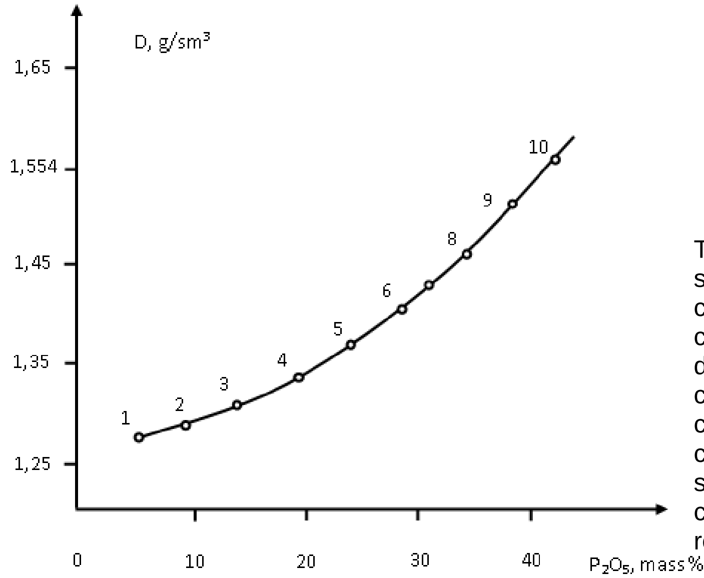

***Fig. 3**. Change in the density of saturated solutions in the* $CuSO_4$-H_3PO_4-H_2O system at 30 ° C

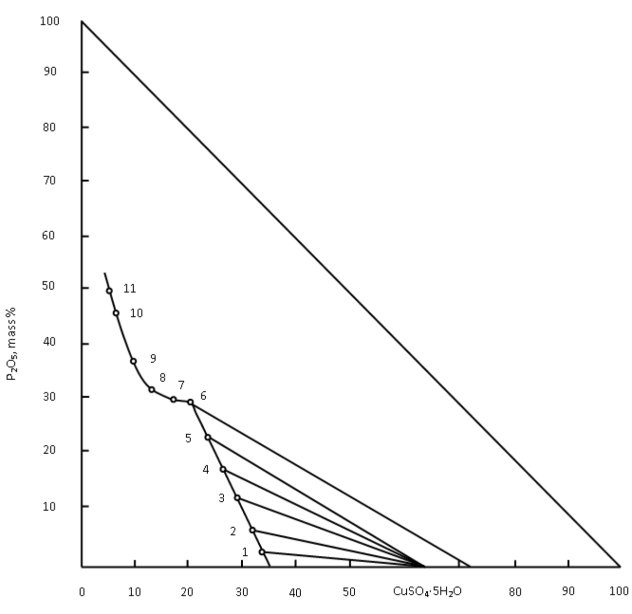

***Fig. 4.** The solubility isotherm of the* $CuSO_4 – H_3PO_4 – H_2O$ *system at 80 ° C*

The first branch of the solubility curve corresponds to saturated solutions, from which copper sulfate pentahydrate crystallizes into the solid phase. With an increase in the concentration of phosphoric acid, the solubility of the salt decreases from 34.94 wt.% To 20.38 wt.%. The second branch corresponds to the formation of a compound of the composition $CuSO_4 \cdot CuHPO_4 \cdot 2H_2O$ in the system. This compound is formed from a saturated solution of copper sulfate in phosphoric acid with a phosphorus anhydride content above 30.42%. Chemical analysis of the precipitate revealed the following composition:

Cu - 35,82; PO_4, - 26,82; SO_4, - 27,15,

which practically corresponds to the compound CuSO4 · CuHPO4 · 2H2O. Theoretically, this compound contains Cu - 35,79; PO_4 - 26,74; SO_4 - 27,05.

3 CONCLUSION

Consequently, the solubility diagram of the system at 30 ° C has one branch, corresponding to the precipitation of $CuSO_4 \cdot 5H_2O$, copper sulfate pentahydrate into the equilibrium solid phase, and the solubility isotherm of the H_3PO_4-H_2O system at 80 ° C consists of two branches : the first branch of the solubility curve corresponds to saturated solutions, from which copper sulfate pentahydrate crystallizes into the solid phase, the second branch corresponds to the formation of a compound of the composition $CuSO_4 \cdot CuHPO_4 \cdot 2H_2O$.in the system.

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