PHYSICO-CHEMICAL PROPERTIES OF MALIN-UROTROPIN-COPPER SULFATE SYSTEM

Aysara A. Orazbayeva[1], Bahtiyor S. Zakirov[1], Bahrom Kh. Kucharov[1], Rima N. Kim[1], Matluba B. Eshpulatova[1], Ziyoda K. Jumanova[2]

[1]*Institute of General and Inorganic Chemistry*
Academy of Sciences of the Republic of Uzbekistan
77a Mirzo Ulugbek, Tashkent 100170, Uzbekistan
[2]*Karakalpak state university named after Berdakh,*
1 Abdirov, Nukus 230100, Uzbekistan
E-mail: ayka-orazbayeva8305@mail.ru

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ABSTRACT

Before seed treatment, the seed must contain several active ingredients. Because the mail significant part of the saved crop depends on the correct seed dressing technology. Seed dressing, or seed treatment with pesticides, is an activity aimed at protecting plants from pests and diseases, using special preparations. In this study, the physicochemical properties of the formalin-urotropine-copper sulfate system were investigated at 25°C. It is established that the isotherms of the system confirmed that the density, viscosity, pH of the solution medium and the crystallization temperature are characterized by inflection points corresponding to concentrations. Analysis of the "composition - properties" diagram of the system shows that the isotherms of the refractive index, density, viscosity and pH of the medium are characterized by two inflection points corresponding to 30 % formalin and 15 % urotropine that equals molar ratio of 1:1:1. Thus, it can be assumed that the interaction of formalin with copper sulfate in aqueous solutions results in the formation of a complex compound of the composition [30 % CH_2O +15 % $C_6H_{12}N_4$]-$CuSO_4\cdot 5H_2O$. Based on the data obtained, a solubility diagram was constructed, identified by X-ray phase, IR spectroscopic and thermogravimetric. Comparison of the value of the degree of crystallinity of the studied samples shows that the degree of crystallinity increases in the samples.

Keywords: diffraction pattern, formalin, urotropine, copper sulfate, X-ray diffraction pattern, solubility.

INTRODUCTION

The development of agriculture at the present stage requires scientific research to expand the spectrum of action of drugs on various harmful objects, reduce their consumption rate, extend the period of protective action and reduce the frequency of treatment, reduce the phytotoxic effect of drugs on plant crops, increase the full germination of seeds and obtain maximum economic benefits from their use.

A significant part of the saved crop depends on the correct seed dressing technology. Despite the high cost of this technology, it is cost-effective. So, seed treatment allows you to save up to 50 % of the crop, which is a necessary condition for the enterprise to achieve high performance [1].

Seed dressing, or seed treatment with pesticides, is an activity aimed at protecting plants from pests and diseases, using special preparations. Fungicidal preparations used for dressing seeds are called protectants. During dressing, pesticides are applied to seeds to neutralize them from external and internal infections of plant origin, as well as to protect seedlings and seeds from pests and phytopathogenic microorganisms living in the soil [1].

Despite the high cost of this technology, it is cost-effective. Because of seed dressing the crop save up to 50 % approximately. This in turn leads to necessary condition for the enterprise to strive for high performance [2].

As seed protectants, several various chemical compounds are used, previously produced inorganic preparations of arsenic and copper [3], sodium hypochlorite, hydrogen peroxide, mercuric chloride [4 - 6]. However, scientific and practical interest is presented organic compounds that do not contain metals [3], but content organic substances such as citric acid [7], *n*-hexane, chloroform, acetone and methanol [8].

Known drugs with one active ingredient of several foreign companies called “Vitavax 200”, “Bronotak”, “Dabron”, “Kisan”, “Montseren” and others used as disinfectants for cotton seeds and cereals to prevent root rot, gummosis, dusty and hard smut [9 - 12].

In the republic, furfuroliden - dicarbamide and monofurfural urea, sodium salts of cotton soapstock, carboxylic and carbolic acids were synthesized from carbamide derivatives, their biological activity against diseases of loose and hard smut, root rot and gummosis of winter wheat and cotton was established [9].

Such preparations for pre-sowing seed treatment successfully destroy pathogens of various plant diseases, fully protect them from infection and pests, and ensure good seed germination. When using such preparations intended for pre-sowing treatment of seeds, due to the presence of several active substances in their composition, where the lack of effectiveness of one active substance with fungicidal or insecticidal activity is compensated by the action of another active substance.

In this regard, a high effect can be obtained when using such preparations, as well as ensuring the normal growth and development of plants during presowing seed treatment, i.e. such drugs have a wide spectrum of action.

To expand the spectrum of action of drugs on various harmful objects, reduce their consumption norm, extend the period of protective action and reduce the frequency of processing, reduce the phytotoxic effect of drugs on crops, increase the full germination of seeds and obtain the maximum economic effect from the use of drugs for presowing seed treatment, they must contain several active ingredients, including plant growth and development stimulators, i.e. have multifunctional complex-acting properties.

EXPERIMENTAL

The experiments were carried out on a laboratory setup consisting of a glass reactor equipped with a stirrer with an electric wire placed in a water thermostat. The rotation speed of the electric motor was controlled by a rheostat and measured with a TM-300N tachometer and an RT-230U electronic relay. Based on the obtained results, the “composition-property” diagrams of the system under study were constructed [13].

X-ray diffraction (XRD) patterns of new compounds were taken on a Shimadzu powder diffractometer (Japan). Crystallinity, sizes of nanoparticles, etc. have been determined [14].

The pH of the solution medium was measured on a FE-20 METTLER TOLEDO pH meter [15].

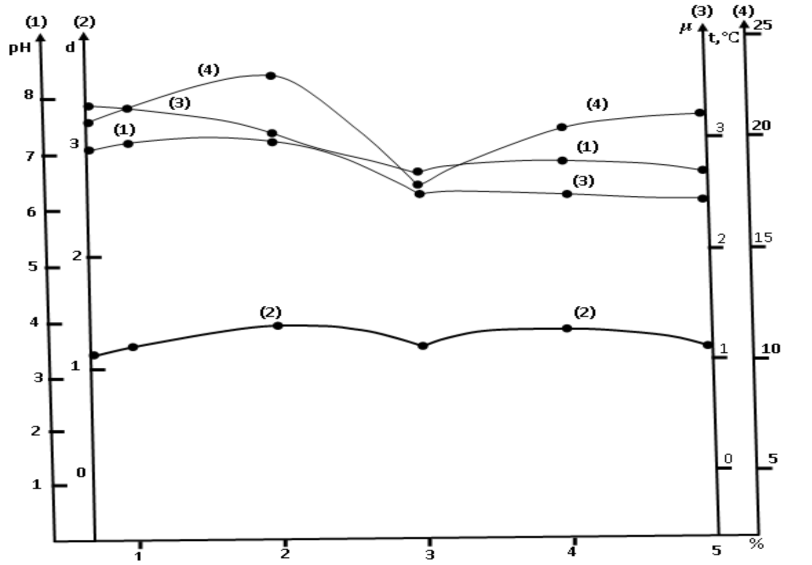
Quantitative chemical analysis was carried out using a quantitative phase analysis by the Rietvelt method. Thermal analysis - Thermo Scientific GC1310 combined Tsq 9000 TA Instilments STD 650 (USA). IR spectroscopy - Perkin Elmer Spectrum Two (USA) [16].

RESULTS AND DISCUSSION

For the physicochemical substantiation of the process of obtaining new seed dressers, we studied the “Composition-Properties” diagram in the formalin-urotropine-copper sulfate system at 250^{o}C. It has been established that when studying the rheological properties of the system, the density, viscosity, pH of the medium of solutions and the crystallization temperature are characterized by inflection points with the corresponding concentrations.

Analysis of the “Composition - properties” diagram of the system shows that the isotherms of the crystallization temperature, density, viscosity and pH of the medium are characterized at one inflection point corresponding to 30 % CH_2O (formalin), 15 % urotropine and 3 % copper sulfate (Fig. 1., Table 1). Thus, it can be assumed that the interaction of formalin with copper sulfate in aqueous solutions results in the formation of a complex compound of the composition $CH_2O \cdot C_6H_{12}N_4 \cdot CuSO_4 \cdot 5H_2O$.

The resulting compound was recovered in solid form and analysed by chemical and physicochemical methods of analysis. The results are presented in Table 2.



30% CH_2O + 15% $C_6H_{12}N_4$ $CuSO_4 \cdot H_2O$

Fig. 1. Composition-property diagram of the formalin-urotropine-copper sulfate system: 1 - medium pH, 2 - density, 3 - viscosity, 4 - crystallization temperature.

Table 1. Physicochemical properties of solutions versus the composition in the systemcomplex salt.

No.	Content of components, %		$t_{average}$, °C	d, g cm^{-3}	μ, mm^2 s^{-1}	pH
	[30 % CH_2O+15 % $C_6H_{12}N_4$]	$CuSO_4$•$5H_2O$				
1	100	-	-21.0	1.20	2.43	6.58
2	98.04	1.96	-21.5	1.20	3.30	7.20
3	96.13	3.87	-23.0	1.35	3.10	7.20
4	94.34	5.66	-18.0	1.15	2.53	6.60
5	92.6	7.40	-20.5	1.30	2.50	6.80
6	90.91	9.09	-21.0	1.10	2.43	6.58

Table 2. Chemical composition of the compound.

Name	Content, %					
	C	N	O	H	S	Cu
Found	20.0	13.33	38.10	5.71	7.62	15.24
$CH_2O \cdot C_6H_{12}N_4 \cdot CuSO_4 \cdot 5H_2O$	20.01	13.35	38.12	5.73	7.64	15.25

When analysing a compound, energy-dispersive scanning electron microscope (SEM-EDX) methods are now widely used to obtain data with high accuracy and increase the reliability of research results to solve specific scientific and technological problems. The amount of nitrogen, sulfur and metals and the resulting compounds were determined using (SEM-EDX).

Fig. 2 presents of the results SEM-EDX analyses. From Fig. 2 seen that compound contents crystals with chemical elements revealed in various colours.

Comparing the data obtained from the XRD analysis of the initial complex salt, it can be noted that all reflections on the diffraction patterns, as a rule, are characterized by their own reflection angles, a set of interplanar distances and diffraction line intensities (Fig. 3 and Table 3). This indicates the individuality of the crystal lattice of the complex salt.

Comparison of the values of the degree of crystallinity of the studied samples shows that the degree of crystallinity increases in the samples.

Thermal analysis represented in Fig. 4 showed that on the heating curve of the derivatogram of the compound of the composition $CuSO_4 \cdot 5H_2O \cdot C_6H_{12}N_4$ of the obtained compound, two endothermic effects are observed at 81.75; 174°C and four exotherms at 331.96; 574.01; 704.22; and 890.64°C. The first two endo-effects are due to the dehydration of the compound, while the weight loss is 2.477 %. The following thermal effects correspond to the decomposition of the substance with a mass loss of 9.695 % at a temperature range

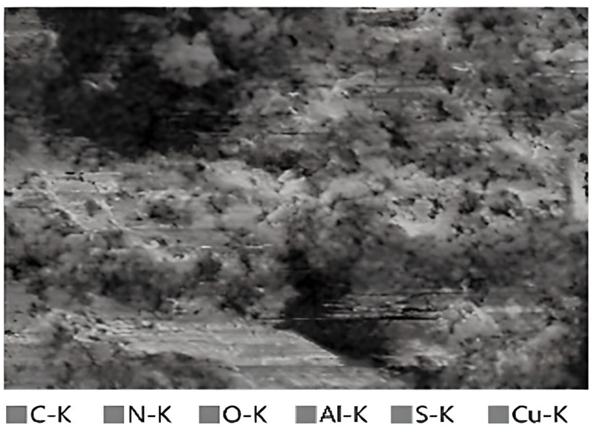


Fig. 2. Microstructure of complex salt compound.

Table 3. Interplanar distances and relative intensities of the complex salt lines.

No.	2Q	d, A°	I, %
1	13.41	6.5999	17.0
2	13.83	6.3980	31.0
3	14.43	6.1333	9.0
4	15.11	5.8607	12.0
5	16.48	5.3747	106.0
6	17.83	4.9707	240
7	19.96	4.4459	8.0
8	20.71	4.2865	47.0
9	22.75	3.9048	71.0
10	24.21	3.6740	14.0
11	25.33	3.5133	15.0
12	27.00	3.2991	7.0
13	27.86	3.2003	28.0
14	30.58	2.9211	14.0
15	31.13	2.8707	29.0
16	33.36	2.6841	48.0
18	35.66	2.5161	100
19	36.53	2.4578	13.0
20	37.73	2.3823	11.0
21	39.68	2.2696	7.0
22	41.31	2.1840	16.0
23	42.18	2.1407	10.0
24	43.33	2.0865	11.0
25	44.61	2.0298	14.0
26	46.13	1.9662	9.0
27	48.41	1.8790	11.0
28	52.61	1.7384	25.0
29	57.78	1.5944	7.0
30	59.18	1.5600	10.0
31	60.18	1.5364	8.0
32	61.58	1.5048	10.0

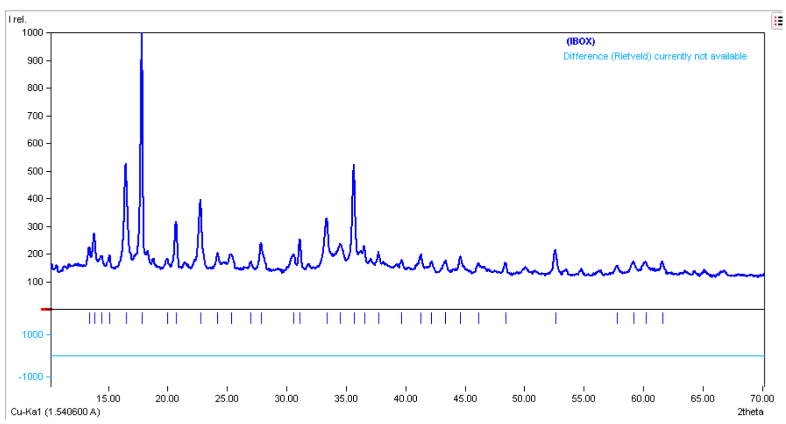


Fig. 3. XRD of the complex salt.

of 120 - 230°C. The nature of subsequent exo-effects at 331.96; 574.01; 704.22; 891°C are associated with the decomposition of urotrapine by the combustion of thermolysis products, the decomposition of copper sulfate to copper oxide (Fig. 4).

To establish the individuality and structure of the complex, we studied the IR spectra of the complex salt (Fig. 5).

Figure shows the infrared spectra of copper complex with methenamine. The reflectance band of complex at 779 cm^{-1}, 1079 cm^{-1}, and between 2700-3200 $cm^{-1}$are attributed to the S-O stretching, S=O stretching, O-H symmetric and asymmetric stretching vibration of $CuSO_4 \cdot 5H_2O$. On the other hand, the reflectance band of complex at 600 cm^{-1} and 492 cm^{-1} are attributed to the C-N stretching, vibration of methenamine.

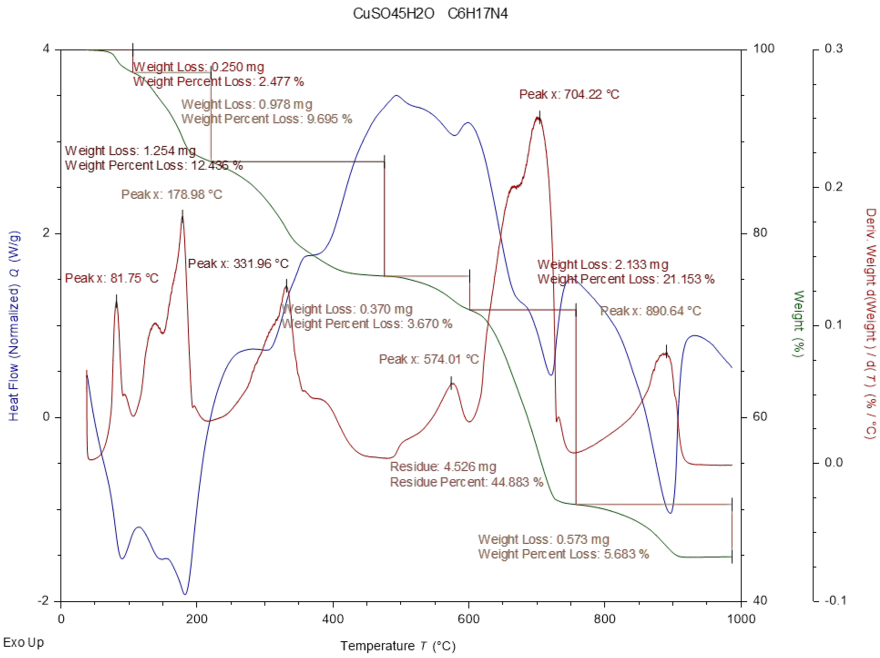


Fig. 4. Derivatogram of the complex salt.

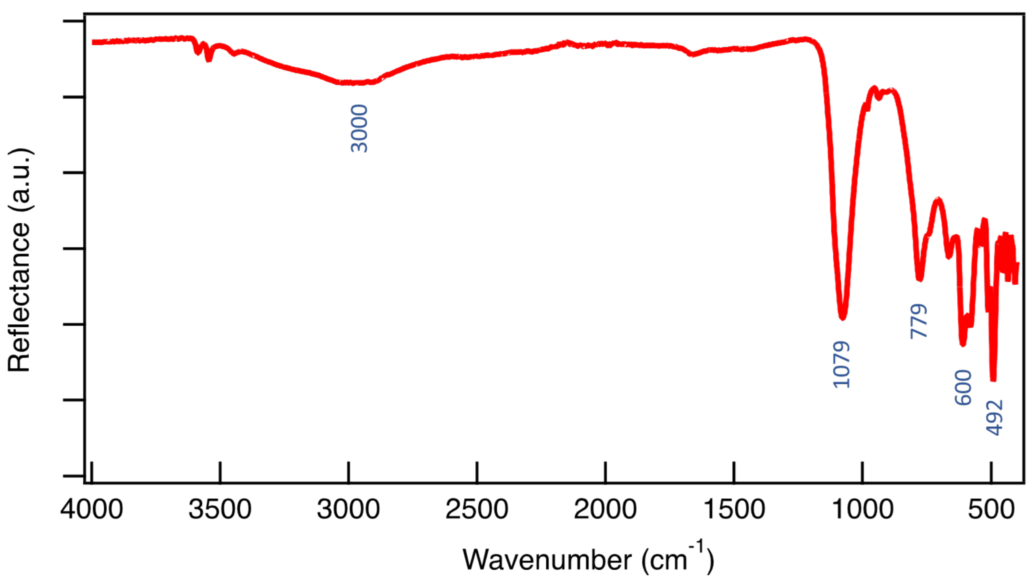


Fig. 5. IR spectrum of complex salt.

CONCLUSIONS

Thus, to achieve the goal - obtaining seed protectants, the "Composition-properties" diagram of the formalin-urotropine-copper sulfate-water system at 25°C was studied. Analysis of the composition-solubility property diagram shows that a new compound of the composition $CH_2O \cdot C_6H_{12}N_4 \cdot CuSO_4 \cdot 5H_2O$ is formed in the system, which is identified by chemical, XRD phase, IR spectroscopic, thermogravimetric methods of analysis, as well as using a scanning electron microscope of energy dispersive analysis (SEM -EDX). Agrochemical and biological tests of the synthesized compound have established that the resulting preparation not only has a fungicidal effect, but also significantly stimulates plant growth, which ultimately contributes to an increase in the yield of raw cotton.

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