Research on the effect of microelement salt with fertilizer

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Abstract. The visual-polythermal method was used to study the solubility of components in the $ZnSO_4 – (NH_4)_2SO_4 – H_2O$ system over the temperature interval of -22.0°C to +36.1°C. Solubility and characteristics of the constituents of the system at different temperatures and concentrations were studied to show the physicochemical interactions between zinc sulfate and ammonium sulfate. The phase description delineates the areas of ice crystallization, $(NH_4)_2SO_4$, $ZnSO_4·(NH_4)_2SO_4·6H_2O$, and $ZnSO_4$. A solubility diagram was drawn and a new compound, $ZnSO_4·(NH_4)_2SO_4·6H_2O$, was isolated. The system $ZnSO_4 – (NH_4)_2SO_4 – H_2O$ was investigated using thirteen inner sections. At the double and triple points of the system, the equipoise composition of solutions and crystallization temperatures were clarified. The analysis was carried out using contemporary physicochemical analysis methods to confirm the identity of the obtained compound. Analytical data on physicochemical changes, thermal stability and chemical decomposition of the $ZnSO_4·(NH_4)_2SO_4·6H_2O$ sample with temperature change were presented. All the diffractographic changes in the X-ray pattern of a new compound, in particular, the set of distances between the planes, the activation of their reflection angles, and the diffraction lines confirm the individuality of the new compound.

1 Introduction

In plant, animal, and human metabolism, each microelement [1, 2] plays a specific role and its deficiency cannot be remedied by substituting another element [3-5]. The amount of nutrients in the soil determines the concentration of nutrients in plant parts and the amount of yield and greatly impacts the health of humans through the consumption of this plant. Globally, about one-third of arable soils are deficient in zinc, affecting the human nutritional system [6]. Consumption of micronutrient-deficient foods leads to factors that negatively affect human health, such as anaemia, reproductive health, reduced growth, and decreased

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cognitive and physical performance [7]. A majority of the population in developing countries suffers from deficiencies in micronutrients [8-10].

It is possible to eliminate microelement deficiency [11-13] by producing organic and inorganic fertilizers containing these elements and applying them to soils and plants [14-17]. For example, when microelements (Zn, Cu, Mn, Fe, Mo, B) and nitrogen fertilizer were applied to clay loam soils of Iran, it was noted that the grain yield of rice increased by 30% [18]. As a result of applying zinc and manganese microelements to corn at a ratio of nitrogen, phosphorus and potassium (NPK) 120:60:40 kg/ha, corn kernels and grain yield grew [19].

It is important to implement trace elements into NPK fertilizers and high-yielding varieties in order to achieve high profits. Among these are zinc, iron, manganese, and boron [20]. Several factors can affect how micronutrient supplements affect fertilizers, including their nature, concentration, and method of application [21-24].

2 Materials and methods

In the research work, water, ammonium sulfate and zinc sulfate were considered research objects, and we used chemically pure ammonium sulfate (GOST 3769-78) and zinc sulfate salt (GOST 4174-77). Our experimental measurements included X-ray phase analysis (LabX XRD-6100, Japan) [25], infrared spectroscopic analysis (PerkinElmer Spectrum IR 10.7.2) [26] and thermal analysis (Linseis STA PT 1600) [27]. Elemental analysis was performed for the nitrogen, zinc, oxygen and sulfur content of zinc-ammonium sulfate hexahydrate (Zeiss EVO MA10) [28]. The phase equilibrium studies were performed using the visual polythermal method [29].

3 Results and discussion

Solubility and characteristics of the constituents of the $ZnSO_4$ – $(NH_4)_2SO_4$ – H_2O system at different temperatures and concentrations were studied to show the physicochemical interactions between zinc sulfate and ammonium sulfate. The system $ZnSO_4$ – $(NH_4)_2SO_4$ – H_2O was investigated using thirteen inner sections (Figure 1). From them, sections I-VIII were studied from the $ZnSO_4$ side to the $(NH_4)_2SO_4$ peak, and sections IX-XIII were studied from the $(NH_4)_2SO_4$ - H_2O side to the $ZnSO_4$ peak. A polythermal solubility diagram of the $ZnSO_4$ – $(NH_4)_2SO_4$ – H_2O system was built in the temperature interval from -22.0°C to +36.1°C based on binary systems and inner cross sections. The crystallization areas of ice, ammonium sulfate, $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, and zinc sulfate are limited in the phase diagram of the system state. These areas come together at two triple points of the system. At the double and triple points of the system, the equipoise composition of solutions and crystallization temperatures were clarified (Table 1).

Table 1. Nodal Points of double and triple of $ZnSO_4$ – $(NH_4)_2SO_4$ – H_2O.

Composition of the liquid phase , %			**Crystallization temperature, °C**	**Solid phase**
$(NH_4)_2SO_4$	$ZnSO_4$	H_2O		
0.2	39.8	60.0	+36.1	$ZnSO_4 \cdot 7H_2O$ + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
0.4	34.8	64.8	+13.2	$ZnSO_4 \cdot 7H_2O$ + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
0.7	29.8	69.5	+8.0	$ZnSO_4 \cdot 7H_2O$ + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
-	27.8	72.2	-6.4	ice + $ZnSO_4 \cdot 7H_2O$

0.8	27.2	72.0	-12.9	ice + $ZnSO_4 \cdot 7H_2O$ + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
0.9	24.8	74.3	-12.7	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
1.1	19.8	79.1	-12.4	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
1.5	14.8	83.7	-12.0	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
1.8	9.8	88.4	-11.8	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
2.0	4.9	93.1	-11.6	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
4.9	5.0	90.1	-10.8	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
9.9	0.4	89.7	-11.0	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
14.9	0.3	84.8	-11.6	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
19.9	0.2	79.9	-13.0	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
24.9	0.3	74.8	-14.9	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
29.4	0.4	70.2	-22.0	ice + $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ + $(NH_4)_2SO_4$
29.6	-	70.4	-19.0	ice + $(NH_4)_2SO_4$

The first three points correspond to 0.8% ammonium sulfate, 27.2% zinc sulfate, and 72.0% water with a crystallization temperature of -12.9°C. In this state, the firm phase is comprised of ice, zinc sulfate heptahydrate, and zinc-ammonium sulfate hexahydrate.

The second triple point corresponds to 29.4% ammonium sulfate, 0.4% zinc sulfate, and 70.2% water at a crystallization temperature of -22.0°C, and the composition of the firm phase is comprised of ice, ammonium sulfate, and zinc-ammonium sulfate hexahydrate.

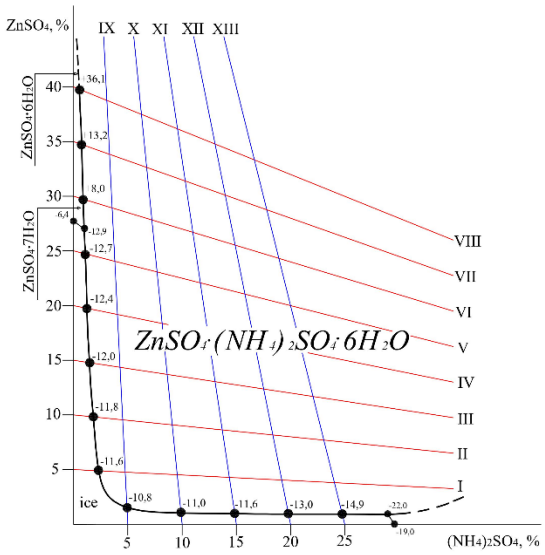

Fig. 1. Polythermal solubility diagram of $ZnSO_4$ – $(NH_4)_2SO_4$ – H_2O system.

The new compound was analyzed chemically and the following results were obtained: found, mass. %: N=7.0; Zn=16.3; S=16.0; O=55.8; H=5.0;

For $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ calculated, mass. %:

N=6.98; Zn=16.2; S=15.9; O=55.9; H=4.9;

To confirm the identity of the obtained compound, the analysis was carried out using contemporary physicochemical analysis methods, and the data are presented based on the following results.

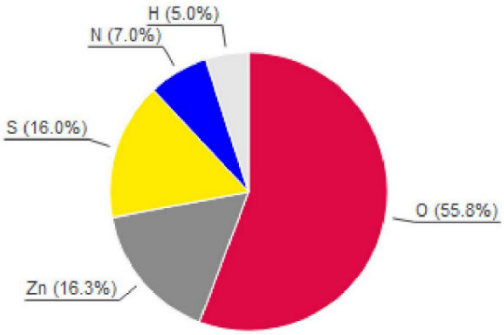

Fig. 2. Chemical analysis of $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

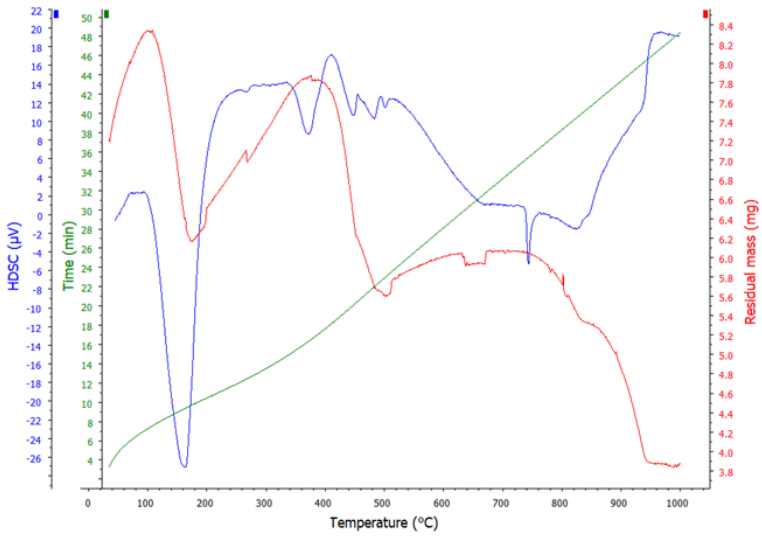

Fig. 3. Thermogram of $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

Analytical data on physicochemical changes, thermal stability and chemical decomposition of the $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ sample with temperature change were presented. After starting the analysis at 350^0C, the lowest endothermic effect was observed at 164^0C due to sharp mass loss, and the highest exothermic effect was observed at 402^0C. In the temperature range from 520°C to 804°C, the endothermic effect occurred due to the stable maintenance of the mass, and the mass decreased by 46% from the initial state to the end of the process. DTA and TGA analyses were performed in an oxidizing medium at a rate of 20 C/min on an STA PT 1600 synchronous thermal analyzer manufactured by Linseis, Germany (Figure 3).

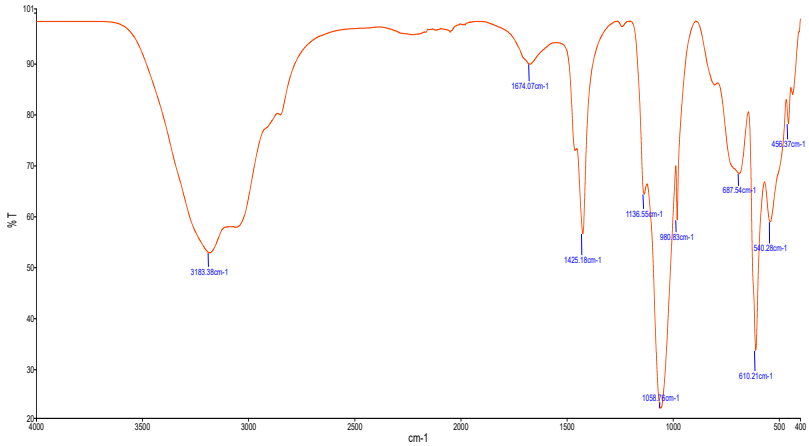

Fig. 4. IR spectrum of $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ compound.

In describing the molecular structure of the new compound and the chemical bonding of the IR spectrum, the following information was given. The lines observed in the 1700-1400 cm^{-1} spectral region of the band indicate that water is strongly bonded to hydrogen in the $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ crystal structure. The H-O-H bending mode is significant in the 1400 cm^{-1} part of the band, which may be because hydrogen bonds in the crystal originate from water molecules or O-H-O bonds in addition to the contribution of amide ions. The band at 3183.38 cm^{-1} represents the stretching vibration of the O-H group bonded to H, the frequency band at 1674.07 cm^{-1} represents H_2O in the strain mode or N-H in the bending mode, and the band at 1425.18 cm^{-1} represents H–O–H in the bending mode or represent N–H vibrations.

In the band region, there are several vibrations of the $SO4^{-2}$ ion, including 1058.76 cm^{-1} asymmetric stretching mode (v_3), 980.83 cm^{-1} symmetric stretching mode (v_1), 687.54 cm^{-1} asymmetric stretching, 610.21 cm^{-1} and 540.28 cm^{-1} represent the bending mode (v_4) and 456.37 cm^{-1} represent the symmetric bending mode (v_2) of the $SO4^{-2}$ ion (Figure 4).

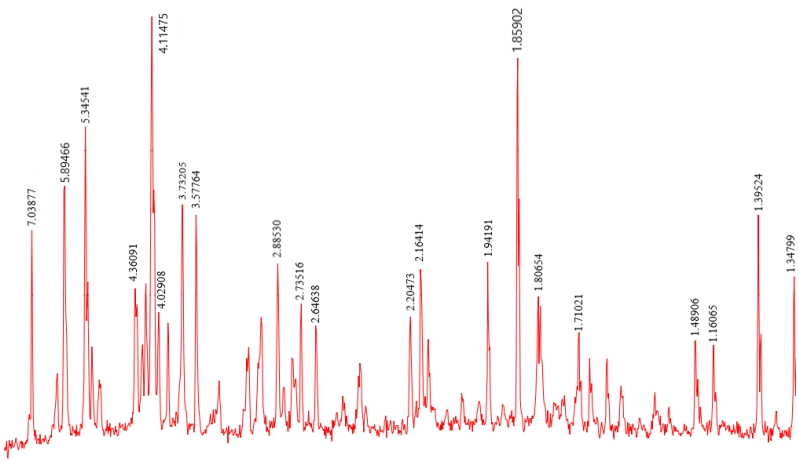

Fig. 5. X-ray pattern of $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

All the diffractographic changes in the X-ray pattern of $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, in particular, the set of distances between the planes, the activation of their reflection angles,

and the diffraction lines confirm the individuality of the new compound. In the radiograph, Å: 1.85902; 4.11475; 5.34541; 5.89466; 1.39524; 3.73205; 3.57764 is above the diffractographic changes, which are consistent with the data from the cited literature.

4 Conclusion

To determine the effective significance of the composition of microelement fertilizers for crop growing, the solubility in the $ZnSO_4$ – $(NH_4)_2SO_4$ – H_2O system was researched by the visual-polythermal method. Physicochemical analysis, including X-ray analysis, IR spectrum, and thermogravimetric analysis, was carried out to confirm the new compound. Our further research will be devoted to the study of the $ZnSO_4$-$NH_4H_2PO_4$-H_2O system.

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