STUDYING THE SOLUBILITY OF THE ZINC SULFATE - AMMONIUM NITRATE - WATER SYSTEM

Dilnoza Ne'matjon qizi Makhkamova[1], Zokirjon Turayev[1],
Ilhom Ikramovich Usmanov[2], Bakhrom Khayrievich Kucharov[3]

[1]Namangan State Technical University,
Uzbekistan, 160115, Namangan, 7 Kasansay St.
dilnozamaxkamova_7007@mail.ru (D.N.M); t-zokirjon@umail.uz (Z.T.)
[2]Karshi State Technical University, Uzbekistan
180100, Kashkadarya region, Karshi, 17 Kuchabog St., BOS@mail.ru (I.I.U.)
[3]The Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan
100170, Tashkent, 77a Mirzo Ulugbek St., Uzbekistan, kucharovbx@gmail.com (B.Kh.K.)

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ABSTRACT

The solubility of the components in the $ZnSO_4$ *-* NH_4NO_3 *-* H_2O *system was studied by the visual-polythermal method in the temperature range from -19.4°C to +13.0°C. The phase diagram delimits the fields of ice crystallization,* NH_4NO_3*,* $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$*, and* $ZnSO_4$*. A solubility diagram was constructed, and a new compound* $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$ *was separated. The new compound was identified by scanning electron microscopy (SEM), chemical, X-ray phase, and IR spectroscopic analysis.*

Keywords: ammonium nitrate, zinc sulfate, $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$*, visual polytherm, X-ray phase analysis, IR spectrum.*

INTRODUCTION

In recent years, the rapid growth of the world's population has significantly increased the demand for food products, creating the need to further develop agriculture, ensure the production of high-yield and high-quality crops, and implement modern agricultural technologies. In this context, the solubility of the $ZnSO_4$ - NH_4NO_3 - H_2O system is of significant practical interest, as its components play an important role in the formulation of micronutrient fertilizers for sustainable agricultural production.

Although plants require trace elements [1 - 3] only in small amounts, their presence significantly enhances crop yield and quality [4, 5]. Each microelement plays a specific role in the metabolism of plants, animals and humans, and their deficiency cannot be compensated for by replacing other elements [6 - 10]. Even though trace elements make up only 0.02 % of the total body weight, they are important as bioactive chemicals or active centers of enzymes [11 - 13].

Micronutrient deficiencies in soil not only reduce crop yields but also degrade the quality of produce [14 - 16].

Micronutrient deficiencies negatively affect the healthy growth and development of plants. As a result of a decrease in the content of essential elements in the soil, leaves lose colour and turn yellow, growth slows down, and productivity decreases. For example, iron deficiency leads to pale leaves (chlorosis), while zinc deficiency causes slow plant growth and small leaves. To eliminate micronutrient deficiencies, it is necessary to increase soil fertility, rational use of microelement-containing fertilizers, and the use of advanced agrotechnical measures [17].

To solve the problem of producing highly effective, complex nitrogen - phosphorus - potassium (NPK) fertilizers, deep physicochemical studies of the interaction of microelements with fertilizer components in the process of their production, storage and the establishment of the mechanism of influence of additives on the properties of the resulting products are required. For physical and chemical substantiation of the process of obtaining NPK fertilizers containing, depending on the ratio of N and solubility in water, potassium chloride, potassium sulfate and ammonium sulfate [18], monoammonium phosphate, urea or ammonium nitrate, the interaction of potassium nitrate [19] was studied and in order to identify the possibility the use of zinc-containing wastes and middling of non-ferrous metallurgy, as well as the chemical industry in the production of mineral fertilizers with the addition of the trace element zinc, the solubility of components in the $ZnSO_4$ - NH_4NO_3 - H_2O system was studied visually by the polythermal method in the temperature range from -19.4°C to +13°C.

EXPERIMENTAL

This study investigated water, ammonium nitrate, and zinc sulfate as the primary research objects. Chemically pure ammonium nitrate (GOST 22867-77) and zinc sulfate (GOST 4174-77) were utilized in the experiments. Analytical techniques comprised X-ray diffraction (LabX XRD-6100, Japan) [20] and infrared spectroscopy (Specord IR-75) [21]. The visual-polythermal method [22] was employed with a TN-6 glass mercury thermometer covering the range from -30°C to 60°C, in combination with the pycnometric method (GOST 31992.1-2012) [23]. The formation of $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$ was confirmed by elemental analysis of nitrogen, zinc, hydrogen, and sulfur using a Zeiss EVO MA10 analyser [24]. Solution viscosity was determined with a VPZh viscometer, and pH measurements were performed using a FE20 METTLER TOLEDO pH meter.

RESULTS AND DISCUSSION

To establish the physicochemical rationale for the formation of zinc-enriched NPK fertilizers utilizing ammonium nitrate as the nitrogen source, the variations in physicochemical parameters of diluted (0.01 M) solutions in the [$ZnSO_4$ (0.01M)] - [NH_4NO_3 (0.01M)] system were systematically investigated as a function of the molar ratio using the isomolar series method.

In the course of the investigation, 0.01 M zinc sulfate and ammonium nitrate solutions were prepared. The zinc sulfate solution was supplemented with successively increasing volumes of the 0.01M NH_4NO_3 solution, after which the resulting mixtures were thermostatted at 20°C. The physicochemical characteristics of the prepared systems, namely pH, refractive index, viscosity, density, and crystallization temperature, were subsequently measured. The obtained data on the variation of these properties as a function of the component ratios in the $ZnSO_4$ - NH_4NO_3 - H₂O system are presented (Fig. 1, Table 1).

The composition - pH diagram revealed that in the [$ZnSO_4$ (0.01M)] and [NH_4NO_3 (0.01M)] system, a gradual decrease in the volume of zinc sulfate solution from 30 mL to 3 mL and a simultaneous increase in the volume of ammonium nitrate solution from 3 mL to 30 mL resulted in a rise in pH values from 3.91 to 6.22. At a pH of 5.01, corresponding to the component ratio [$ZnSO_4$ (0.01M)]:[NH_4NO_3 (0.01M)] = 6:4, a distinct turning point was observed. Such variation in pH within the [$ZnSO_4$ (0.01M) + NH_4NO_3 (0.01M)] system indicates the formation of a new compound.

The study of the crystallization temperature in the [$ZnSO_4$ (0.01M)]:[NH_4NO_3 (0.01M)] system showed that, up to the component ratio [$ZnSO_4$ (0.01 M)]:[NH_4NO_3 (0.01 M)] = 6:4, the temperature rises linearly from -1°C to 0°C. At -0.5°C, a distinct inflection point in the crystallization curve was identified.

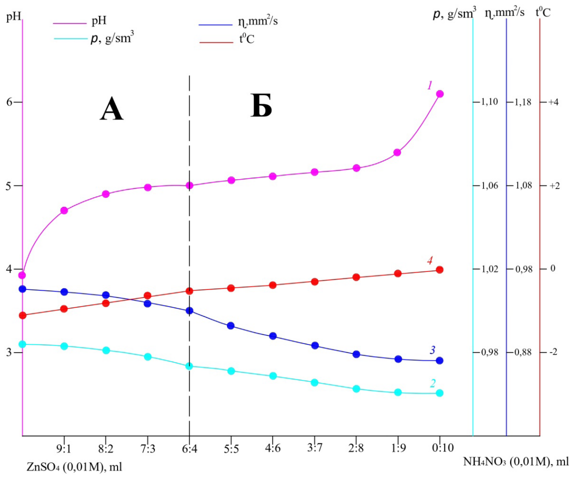

Fig. 1. Changes in pH (1), density (2), viscosity (3), and crystallization temperature (4) of solutions depending on the composition of the components in the system [$ZnSO_4$ (0.01M) + NH_4NO_3 (0.01M)].

Table 1. Changes in the physicochemical properties of solutions depending on the ratio of components in the system [$ZnSO_4$ (0.01M) + NH_4NO_3 (0.01M)].

№	Content of components, mL		pH	Density g cm^{-3}	Viscosity, mm^2 s^{-1}	Crystallization temperature, °C
	$ZnSO_4$	NH_4NO_3				
1	30	0	3.91	0.9846	0.956	-1
2	27	3	4.71	0.9832	0.953	-0.9
3	24	6	4.90	0.9808	0.948	-0.8
4	21	9	4.96	0.9776	0.939	-0.6
5	18	12	5.01	0.9736	0.931	-0.5
6	15	15	5.06	0.9712	0.912	-0.4
7	12	18	5.10	0.9681	0.899	-0.4
8	9	21	5.15	0.9656	0.889	-0.3
9	6	24	5.21	0.9624	0.879	-0.2
10	3	27	5.41	0.9608	0.872	-0.1
11	0	30	6.22	0.9604	0.869	0

Analysis of the "composition - density" relationship showed that increasing the volume of 0.01 M ammonium nitrate solution while reducing the amount of 0.01 M zinc sulfate solution leads to a notable decline in solution density, dropping from 0.9846 g cm^{-3} to 0.9604 g cm^{-3}. At the component ratio [$ZnSO_4$ (0.01 M)]:[NH_4NO_3 (0.01 M)] = 6:4, the density curve displays a distinct inflection point corresponding to a value of 0.9736 g cm^{-3}.

In the "composition - viscosity" diagram, a reduction in the volume of 0.01 M zinc sulfate accompanied by an increase in the amount of 0.01 M ammonium nitrate results in a gradual decrease in solution viscosity from 0.956 mm^2 s^{-1} to 0.869 mm^2 s^{-1}. An inflection point is observed at the component ratio [$ZnSO_4$ (0.01M)]:[NH_4NO_3 (0.01M)] = 6:4, corresponding to a viscosity of 0.931 mm^2 s^{-1}. The obtained results on the physicochemical properties of diluted solutions in this system clearly indicate that at the 6:4 ratio, a change in the mixture's composition occurs.

The $ZnSO_4$ - NH_4NO_3 - H_2O system was examined through fourteen internal sections (Fig. 2). Sections I - VI were plotted from the NH_4NO_3 apex towards the $ZnSO_4$ - H_2O boundary, while sections VII - XIV extended from the $ZnSO_4$ apex to the NH_4NO_3 - H_2O boundary. Using the data from both the binary

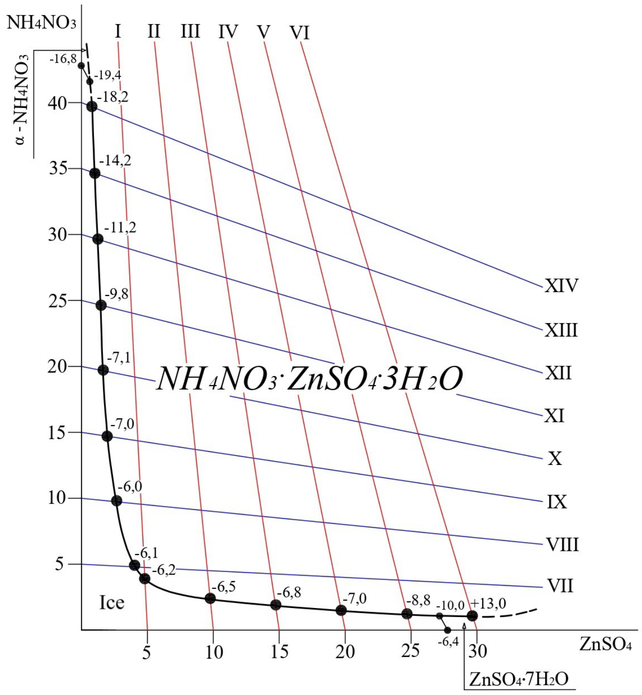

Fig. 2. Polythermal solubility diagram of the zinc sulfate - ammonium nitrate - water system.

Table 2. Double and triple points of the ammonium nitrate - zinc sulfate - water system.

Composition of the liquid phase, %			Crystallization temperature, °C	Solid phase
NH_4NO_3	$ZnSO_4$	H_2O		
-	42.8	57.2	-16.8	ice+α-NH_4NO_3
0.8	41.5	57.7	-19.4	ice+α-NH_4NO_3+$NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
0.8	39.9	59.3	-18.2	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
1.0	34.8	64.2	-14.2	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
1.1	29.8	69.1	-11.2	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
1.2	24.8	74.0	-9.8	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
1.5	19.8	78.7	-7.1	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
2.0	14.7	83.3	-7.0	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
2.4	9.8	87.8	-6.0	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
4.4	4.8	90.8	-6.1	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
4.8	4.1	91.1	-6.2	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
9.7	2.4	87.9	-6.5	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
14.7	1.6	83.7	-6.8	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
19.8	1.3	78.9	-7.0	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
24.8	1.1	74.1	-8.8	ice + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
27.2	1.0	71.8	-10.0	ice+$ZnSO_4 \cdot 7H_2O$+$NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$
27.8	-	72.2	-6.4	ice + $ZnSO_4 \cdot 7H_2O$
29.8	1.0	69.2	+13.0	$ZnSO_4 \cdot 7H_2O$ + $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$

subsystems and the internal sections, a polythermal diagram of the $ZnSO_4$ - NH_4NO_3 - H_2O system was constructed, covering the temperature interval from -19.4°C to +13°C.

The phase diagram of the $ZnSO_4$ - NH_4NO_3 - H_2O system clearly delineates the crystallization regions of ice, ammonium nitrate, and zinc sulfate. These domains converge at two distinct triple points, as summarized (Table 2).

The first triple point of the $ZnSO_4$ - NH_4NO_3 - H_2O system is observed at a composition of 57.7 % H_2O, 0.8 % NH_4NO_3, and 41.5 % $ZnSO_4$, corresponding to a crystallization temperature of -19.4°C. The equilibrium solid phase at this point is represented by ice, the α-modification of ammonium nitrate, and a newly formed compound, $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$. The second triple point occurs at 27.2 % NH_4NO_3, 1.0 % $ZnSO_4$, and 71.8 % H_2O with a crystallization temperature of -10.0°C, where the solid phase consists of ice, zinc sulfate heptahydrate, and $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$.

The isolated new phase formed in the $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$ compound system was studied using a scanning electron microscope, X-ray phase, and IR spectroscopic analysis methods.

In the X-ray diffraction pattern of $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$, the corresponding values for the peaks at 7.09070 Å; 5.89931 Å; 5.30946 Å; 4.21255 Å; 4.13985 Å; 3.74460 Å; 3.58250 Å; 2.79012 Å; 2.39083 Å; 2.20547 Å were 3; 17; 100; 7; 10; 28; 6; 12; 7; 4 % (Fig. 5).

The obtained X-ray results were analysed based on the Mikhaev radiometric index and the American ASTM card table. Based on the obtained X-ray data, it can be said that all diffraction changes, such as the set of diffraction lines, the distances between the planes and their reflection angles, reflect the individuality of

Table 3. Results of chemical analysis of the compound $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$.

<table>
<tr><td rowspan="8">$ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$</td><td colspan="10">Elemental composition of the compound</td></tr>
<tr><td colspan="2">zinc</td><td colspan="2">nitrogen</td><td colspan="2">oxygen</td><td colspan="2">sulfur</td><td colspan="2">Hydrogen</td></tr>
<tr><td>g</td><td>mass, %</td><td>g</td><td>mass, %</td><td>g</td><td>mass, %</td><td>g</td><td>mass, %</td><td>g</td><td>mass, %</td></tr>
<tr><td>65.38</td><td>22.1</td><td>28.0</td><td>9.47</td><td>159.9</td><td>54.1</td><td>32.07</td><td>10.8</td><td>10.0</td><td>3.41</td></tr>
<tr><td colspan="10">Anhydrous elemental composition of the compound</td></tr>
<tr><td colspan="2">zinc</td><td colspan="2">nitrogen</td><td colspan="2">oxygen</td><td colspan="4">sulfur</td></tr>
<tr><td>g</td><td>mass, %</td><td>g</td><td>mass, %</td><td>g</td><td>mass, %</td><td colspan="2">g</td><td colspan="2">mass, %</td></tr>
<tr><td>65.38</td><td>23.8</td><td>28.0</td><td>11.2</td><td>159.99</td><td>56.0</td><td colspan="2">32.07</td><td colspan="2">9.0</td></tr>
</table>

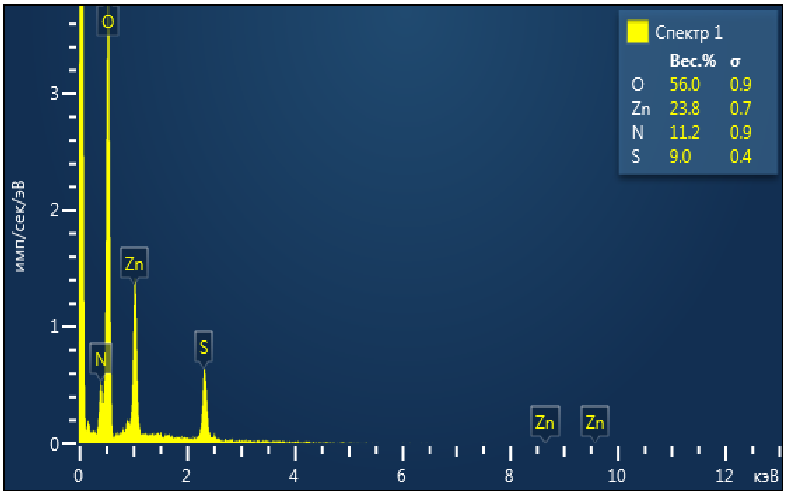

Fig. 3. Quantitative analysis of the compound $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$ using scanning electron microscopy (SEM).

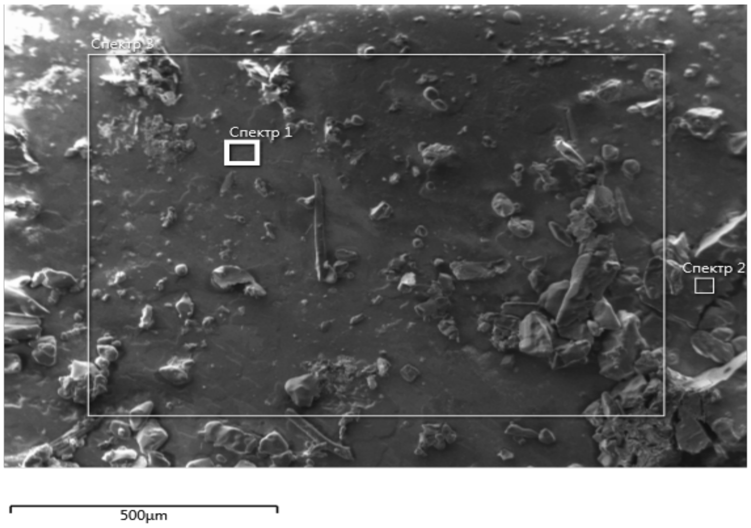

Fig. 4. Enlarged image of the compound $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$ obtained by scanning electron microscope (SEM).

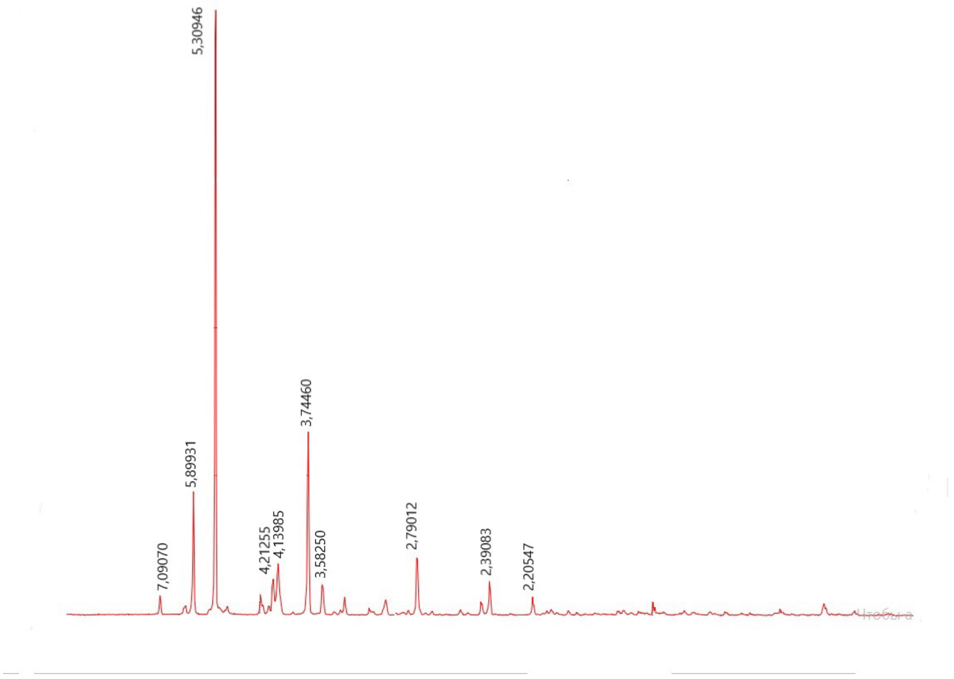

Fig. 5. X-ray phase analysis of the compound $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$.

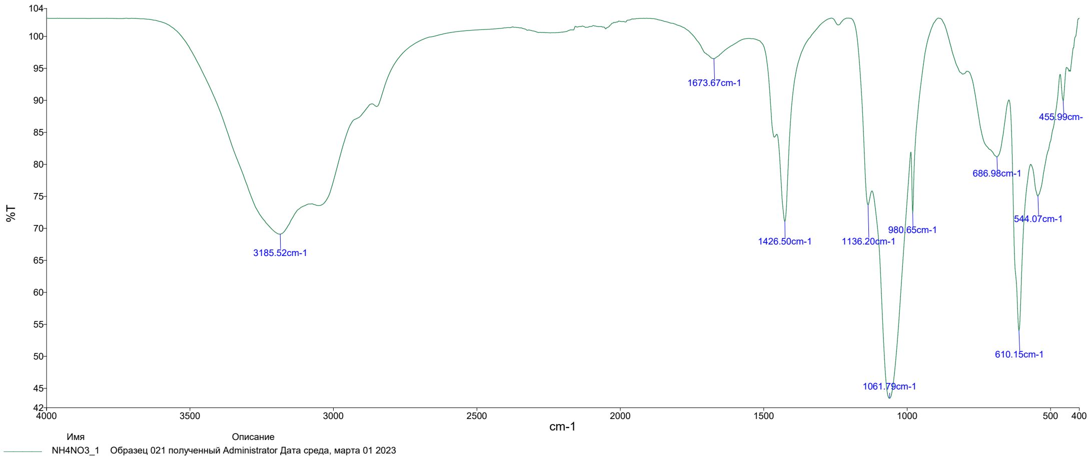

Fig. 6. IR spectrum of the compound $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$.

the $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$ compound.

When studying the absorption lines of various functional groups in the IR spectrum of the crystal structure of $ZnSO_4 \cdot NH_4NO_3 \cdot 3H_2O$, it is seen that a wide vibrational range of the O-H hydrogen bond is expressed in the region of 3185.20 cm^{-1}. In the infrared absorption lines, the frequency range of 1426.50 cm^{-1} is a degenerate deformation vibration of the NH^{+4} group, and the wavelength region of 400-600 cm^{-1} represents the vibrational bonds of Zn-O. The lines of asymmetric stretching 1061.79 cm^{-1} and 1136.20 cm^{-1}, symmetric stretching 980.65 cm^{-1}, absorption 610.15 cm^{-1}, and 686.98 cm^{-1}, are the absorption lines belonging to this SO_4^{-2} group in the bending mode (Fig. 6).

CONCLUSIONS

The study investigated the $ZnSO_4$ - NH_4NO_3 - H_2O system to understand the formation of zinc-enriched NPK fertilizers and the new compound $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$. An inflection point was observed at $[ZnSO_4]:[NH_4NO_3]$ = 6:4, indicating the formation of a new phase because of changes in component ratios, including pH, density, viscosity, and crystallization temperature. As a result of polythermal analysis, two triple points were identified, confirming the coexistence of $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$ with ice, ammonium nitrate, and zinc sulfate. The composition and structure of the new compound were validated through elemental analysis, scanning electron microscopy, X-ray diffraction, and IR spectroscopy. These results indicate optimal conditions for the formation of $NH_4NO_3 \cdot ZnSO_4 \cdot 3H_2O$ and serve as a basis for the development of zinc-enriched NPK fertilizers. In future studies, the solubility and interaction of EDTA-chelated zinc with fertilizer components will be investigated to further optimize the production of micronutrient-rich nitrogen, phosphorus, and potassium fertilizers.

Authors' contributions

D.N.M.: conceptualization, investigation, writing - original draft preparation; Z.T.: methodology, formal analysis; I.I.U.: data curation, validation; B.Kh.K.: review and editing.

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