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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Physicochemical Properties of a Microelement Fertilizer with Amino Acids

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Abstract—The physicochemical properties of the initial components and products were studied with the aim of production of a microelement fertilizer with an amino acid concentrate. The physicochemical properties of the amino acid concentrate and its influence on the stability and sorption properties of fertilizers enriched in microelements were studied.

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Intensification of agriculture requires using not only effective mineral fertilizers containing macro- and microelements [1, 2], but also physiologically active substances, growth stimulants. In the past years, much attention was given to testing as growth stimulants various synthetic and natural physiologically active substances: citric acid, humates, amino acids, etc. [3–6].

The use of amino acids is most often recommended under critical conditions of plant growth: after transplantation, in the flowering period, and also at climatic stresses (night frosts, drought) or plant diseases. Amino acids are particularly effective in fertilizers when used in combination with microelements [7–12].

In this study we examined the physicochemical properties of the amino acid concentrate (AAC) and its effect on the stability and sorption properties of fertilizers enriched in microelements.

As AAC we used Naturamin-WSP product (DAYMSA, Spain), and as fertilizer, ARVI-micro product (ARVI and Co., Lithuania) containing ammonium sulfate and microelements.

The compositions of substances were determined by chemical and physicochemical methods of analysis. The nitrogen concentration was determined by standard methods [13, 14]. The solid substances were examined by IR spectroscopy, thermal analysis, and X-ray phase analysis [15–18]. The IR spectra were recorded on a Spectrum GX FTIR spectrometer (Perkin–Elmer); samples were prepared as KBr pellets. Thermal analysis was performed by differential scanning calorimetry (DSC) with a Du Pont Instruments 990 Thermal Analyzer at a heating rate of 10 deg min^{-1}. X-ray phase analysis was performed with a DRON-6 diffractometer (Ni-filtered Cu radiation, range of diffraction angles 0°–166.5°, relative error ≤0.5%).

Naturamin-WSP amino acid concentrate was prepared by chemical hydrolysis of proteins, collagen, and keratin. The chemical formula of the product depends on the ratio of free amino acids and oligopeptides. Naturamin-WSP product is a concentrate of water-soluble amino acids containing 80% free amino acids and 12.8% nitrogen; the total weight fraction of organic matter is 90%.

Naturamin-WSP concentrate is a homogeneous mixture of microgranules; it contains 17 amino acids in amounts shown in Fig. 1.

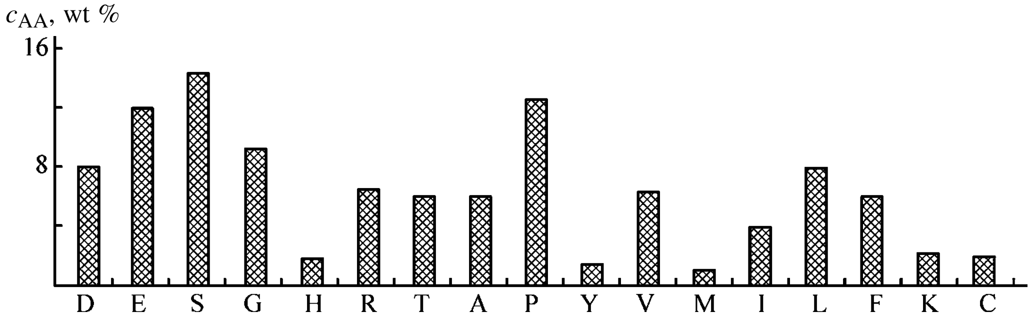

Fig. 1. Content of amino acids c_{AA} in Naturamin-WSP: (D) aspartic acid, (E) glutamic acid, (S) serine, (G) glycine, (H) histidine, (R) arginine, (T) threonine, (A) alanine, (P) proline, (Y) tyrosine, (V) valine, (M) methionine, (I) isoleucine, (L) leucine, (F) phenylalanine, (K) lysine, and (C) cysteine.

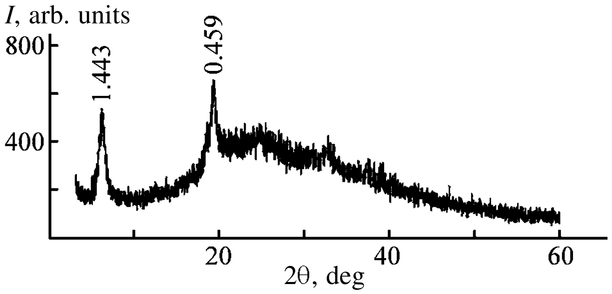

Fig. 2. X-ray diffraction pattern of Naturamin-WSP amino acid concentrate: (*I*) intensity and (2θ) Bragg angle; the same for Fig. 6.

The X-ray diffraction pattern of Naturamin-WSP is shown in Fig. 2; the TG and DSC curves, in Fig. 3; and the IR spectrum, in Fig. 4.

The X-ray diffraction pattern of ACC amino acids (Fig. 2) is typical of amorphous compounds. Only the reflections at 1.443 and 0.449 nm of similar intensity are pronounced; other reflections cannot be identified.

The DSC and TG curves of ACC (Fig. 3) show that, starting from 70°C, Naturamin-WSP loses moisture (TG curve) and remains virtually stable up to ~210°C. At 214.1°C, a pronounced endothermic effect is observed, followed by weight loss. Further heating causes decomposition of the substance (DSC curve exhibits exothermic peaks at 339.0 and 350.0°C, and endothermic peaks at 293.5 and 305.4°C). In the crystalline state, amino acids exist in the form of bipolar ions; their IR spectra (Fig. 4) are similar irrespective of the position of carboxy and amino groups and of the functional substituent. The NH_2 bands are observed at 3500–3000 cm^{-1}; a characteristic C=O band, at 1590–1650 cm^{-1}; and bands of CH, NH_2, and COO^- groups, in the range 1520–450 cm^{-1}.

We studied gravimetrically [13] the sorption of water on AAC under ambient conditions (20–22°C, humidity 25–37%) and in a desiccator over water (~21°C, humidity ~98%). The dynamic curves of water sorption by AAC are shown in Fig. 5.

Under ambient conditions (Fig. 5, curve *1*), AAC takes up a small amount of water (up to 5% in 69 days). Small oscillations of the dynamic curves arise from fluctuations of the ambient temperature and humidity. In a desiccator over water, AAC concentrate absorbs water more actively. Point *a* in curve *2* corresponds to the limiting content of water after which AAC starts to dissolve. Point *b* corresponds to the appearance of mold. Thus, AAC is a hydrophilic substance, and the water absorption depends on the humidity of the medium. This property should be evaluated when using amino acids in production of mineral fertilizers.

For agrochemical and economic reasons, we prepared fertilizers based on ARVI microfertilizer and Naturamin-WSP AAC. ARVI microfertilizer containing 14% nitrogen consists of ammonium sulfate and microcomplex (Mg, S, Mn, Cu, Zn, B, Mo). To this substance we added 1, 3, and 4% AAC and mechanically mixed the components. Therefore, it was necessary to study possible interactions between the components and the stability of the composition. The separate components, ARVI microfertilizers, and ARVI microfertilizers with various additions of AAC were subjected to X-ray diffraction, thermal, and IR analyses (Figs. 6–8).

In the X-ray diffraction pattern of ammonium sulfate (Fig. 6, pattern *1*), we identified its characteristic reflections at 0.519, 0.433, 0.389, 0.314, 0.305,

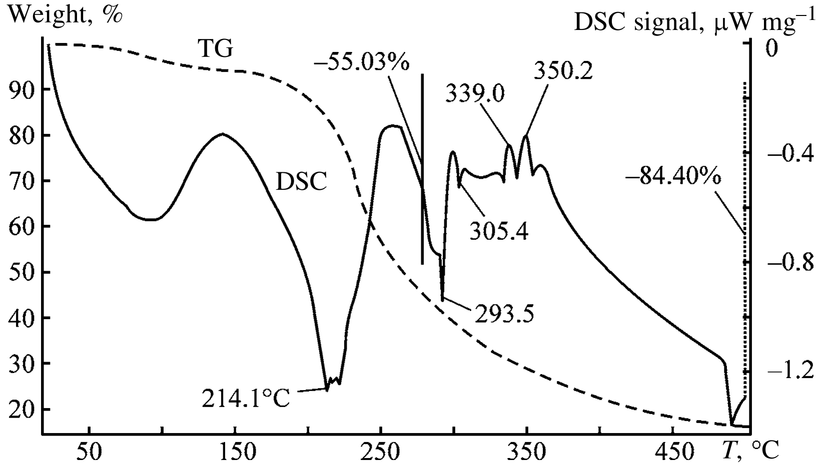

Fig. 3. DSC and TG curves of Naturamin-WSP AAC; (*T*) temperature; the same for Fig. 7.

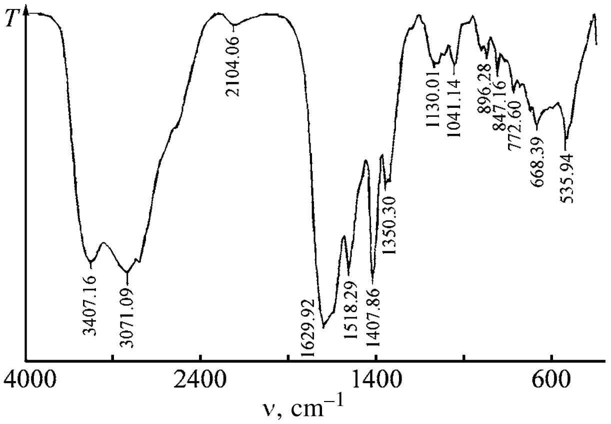

Fig. 4. IR spectrum of Naturamin-WSP AAC: (*T*) transmission and (ν) wavenumber; the same for Fig. 8.

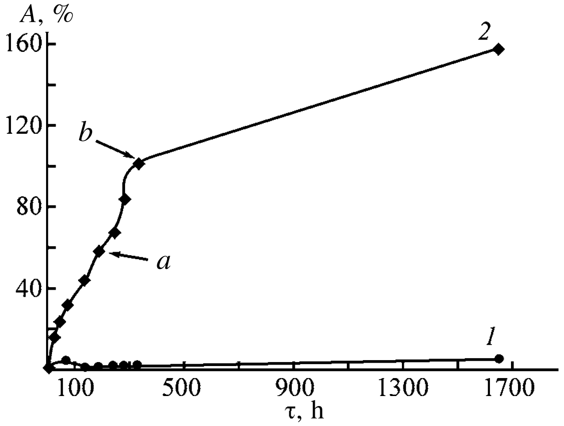

Fig. 5. Dynamic curve of water sorption *A* by AAC (*1*) under ambient conditions and (*2*) in a desiccator over water. (τ) Time; the same for Figs. 9 and 10.

0.299, 0.266, 0.252, 0.232, 0.217, 0.194, 0.177, and 0.164 nm. The microcomplex consists of sulfates of microelements and their crystal hydrates, and also of boric acid; therefore, its diffraction pattern (Fig. 6, pattern *2*) contains reflections of magnesium, manganese, copper, and zinc sulfates and of boric acid at 0.754, 0.598, 0.534, 0.470, 0.447, 0.421, 0.378, 0.341, 0.317, 0.299, 0.287, 0.267, 0.225, 0.220, 0.209, 0.195, and 0.179 nm. The diffraction pattern of ARVI microfertilizer (Fig. 6, pattern *3*) contains reflections of ammonium sulfate and the microcomplex. The diffraction patterns of ARVI microfertilizer with addition of 1, 3, and 4% AAC (Fig. 6, patterns *4*–*6*) exhibit reflections of ammonium sulfate, sulfates of microelements, and AAC. No new reflections are observed, which indicates that the mixture is stable and no chemical reactions occur between the fertilizer components.

The results of thermal analysis are given in Fig. 7. The DSC curve of ammonium sulfate (Fig. 7a) dem-

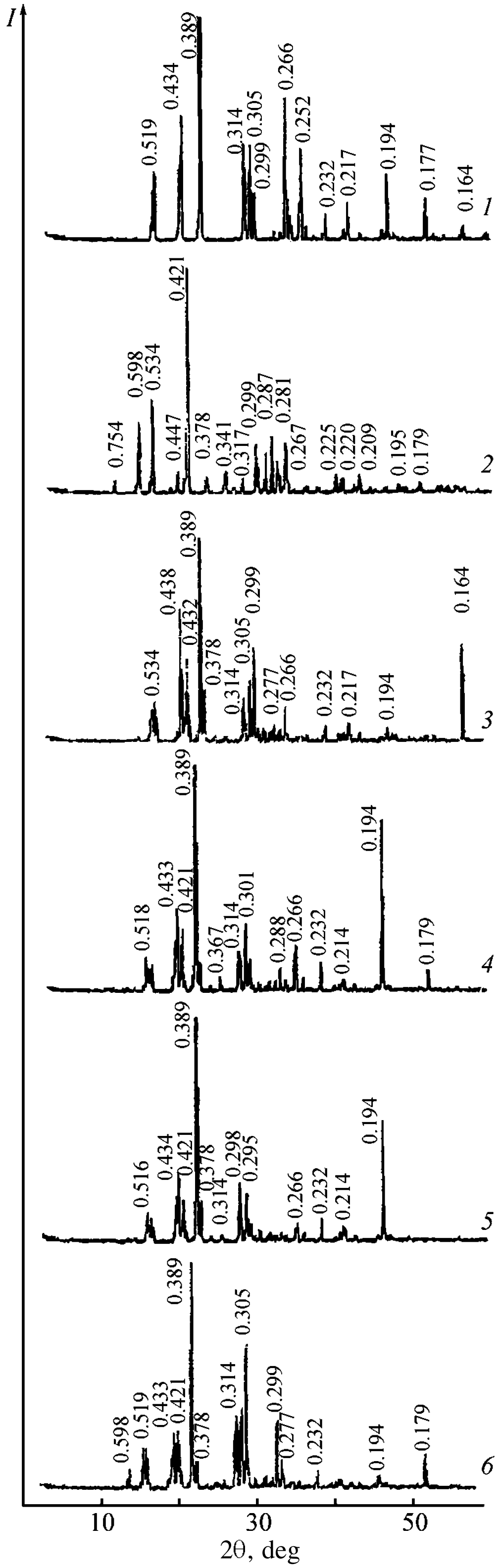

Fig. 6. X-ray diffraction patterns of (*1*) ammonium sulfate, (*2*) microcomplex, (*3*) ARVI microfertilizer, and (*4*–*6*) the same + 1, 3, and 4% AAC, respectively.

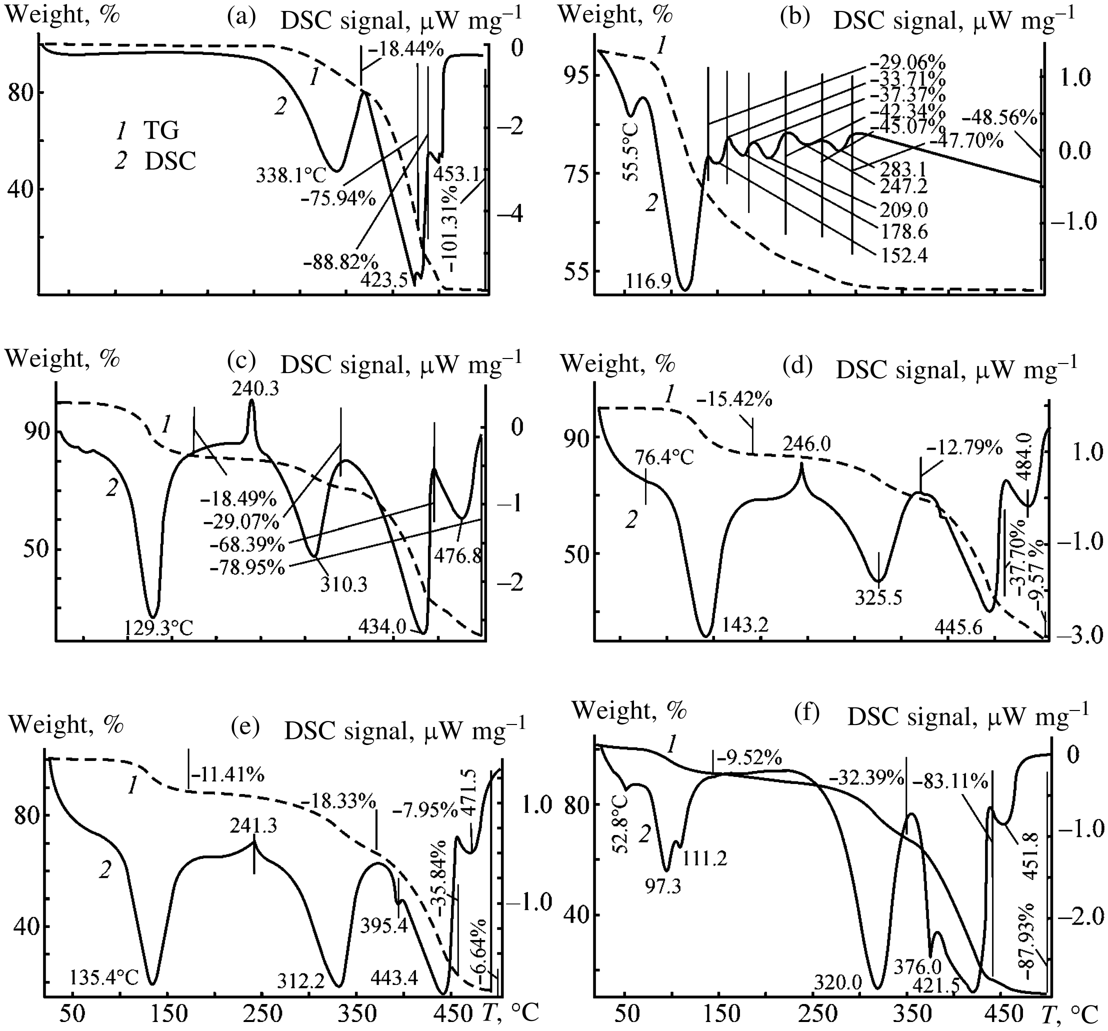

Fig. 7. (*1*) TG and (*2*) DSC curves of (a) ammonium sulfate, (b) microcomplex, (c) ARVI microfertilizer, and (d–f) the same + 1, 3, and 4% AAC, respectively.

onstrates endothermic decomposition of the compound into gaseous ammonia and an acidic salt, NH_4HSO_4. The decomposition starts at about 300 and is complete at 455°C. The weight loss observed in the TG curve is consistent with the elimination of ammonia.

The DSC curve of the microcomplex (Fig. 7b) exhibits an endothermic peak at 55.5°C indicative of the dehydration of boric acid to metaboric acid HBO_2 followed by further dehydration to boron oxide B_2O_3. A pronounced endothermic effect at 116.9°C corresponds to the onset of dehydration of magnesium, manganese, copper, and zinc sulfate crystal hydrates. The effect is complete at 283.1°C. The anhydrous salts remain stable up to 600°C. A continuous weight loss starting about 100°C corresponds to the dehydration.

Thermal analysis of ARVI microfertilizer (Fig. 7c) reveals a total endothermic effect (DSC curve) in combination with weight loss (TG curve) from the initial components, ammonium sulfate and the microcomplex. The DSC and TG curves of ARVI microfertilizer with 1, 3, and 4% AAC (Figs. 7d–7f) exhibit the same peaks as in the curves for the separate components. Some changes in the peak intensities and positions (some of peaks overlap) are natural and insignificant; thus, mixing of the components involves no chemical reactions, and no new chemical compounds are formed.

The IR spectra of the initial substances, ARVI microfertilizer, and ARVI microfertilizer with additions of AAC are shown in Fig. 8. In the IR spectrum of ammonium sulfate (Fig. 8, curve *1*) there are characteristic absorption bands of the NH_4^+ ion at 3000, 2000, and 1400 cm^{-1} and of the SO_4^{2-} ion at 1150–450 cm^{-1}. Since the microcomplex contains a number of sulfates, in its IR spectrum there are strong absorption bands of SO_4^{2-} at 1150–450 cm^{-1}. Also present are bands of boric acid at 1490–1428 cm^{-1} and a weak band at 2400–3000 cm^{-1} assignable to the bridging BH group.

The IR spectrum of ARVI microfertilizer (Fig. 8, spectrum *3*) exhibits characteristic absorption bands of both ammonium sulfate and the microcomplex.

The IR spectra of ARVI microfertilizer with AAC additions are shown in Fig. 8, curves *4–6*. The spectra exhibit characteristic absorption bands of ammonium sulfate, microcomplex, and AAC. In the frequency range 3500–3000 cm^{-1} there are absorption bands of the NH_2 group, and a band at 1590–1650 cm^{-1} corresponds to the C=O bond. Bands at 1520–450 cm^{-1} are characteristic of the NH_2, CH_2, and COO^- groups. All the absorption bands in spectra *4–6* are observed at the same (or slightly shifted) positions as in the spectra of the separate components (ammonium sulfate, microcomplex, AAC); therefore, we can conclude that no chemical reactions occur in ARVI microfertilizers.

To evaluate the sorption properties, we examined the hygroscopicity of the separate components, ARVI microfertilizers, and ARVI microfertilizers with AAC additions under the same conditions as in the above-described AAC tests. The dynamic sorption curves are shown in Figs. 9 and 10.

Experiments on the water absorption under ambient conditions (Fig. 9; 20–22°C, 25–37% humidity) show that only ammonium sulfate (Fig. 9, curve *6*) slightly absorbs water, whereas the other components and fertilizers with AAC (curve *2–5*), especially the microcomplex (curve *1*), even lose moisture.

In a desiccator over water (~21°C, ~98% humidity), all the samples show a linear dependence of the water absorption on time (Fig. 10). In 192 h, the samples start to dissolve, and on samples with AAC a mold appears in 336 h. The lowest water absorption is shown by the microcomplex (curve *1*). All the other substances (ammonium sulfate, ARVI microfertilizers, ARVI microfertilizers with 1, 3, and 4% AAC) take up considerably larger amount of water. The dynamic sorption curves of the fertilizers with AAC resemble that of ammonium sulfate (Fig. 10, curve *2*), which is the major component of the fertilizers.

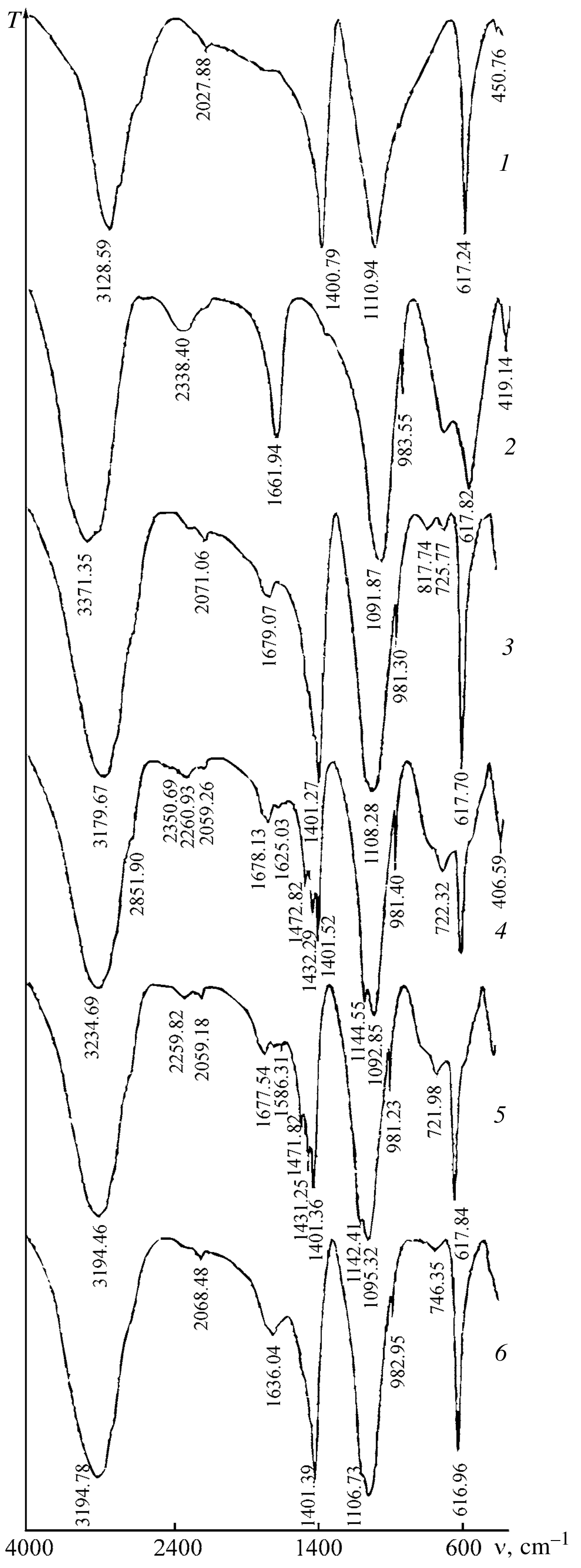

Fig. 8. IR spectra of (*1*) ammonium sulfate, (*2*) microcomplex, (*3*) ARVI microfertilizer, and (*4–6*) the same + 1, 3, and 4% AAC, respectively.

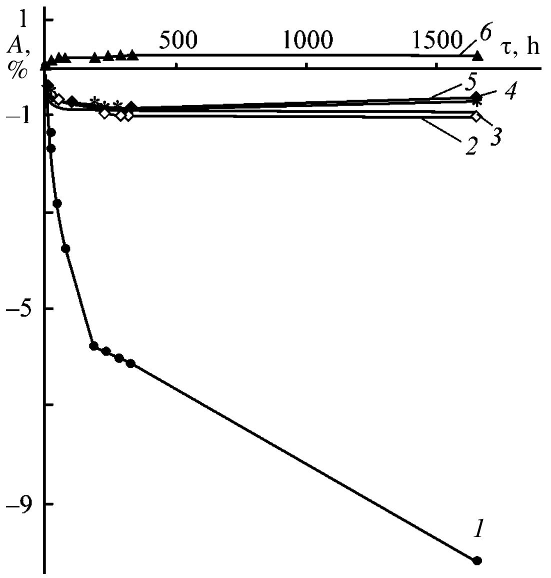

Fig. 9. Dynamic curves of water absorption *A* under ambient conditions by (*1*) microcomplex; (*2*) ARVI microfertilizer; (*3–5*) the same + 1, 3, and 4% AAC, respectively; and (*6*) ammonium sulfate.

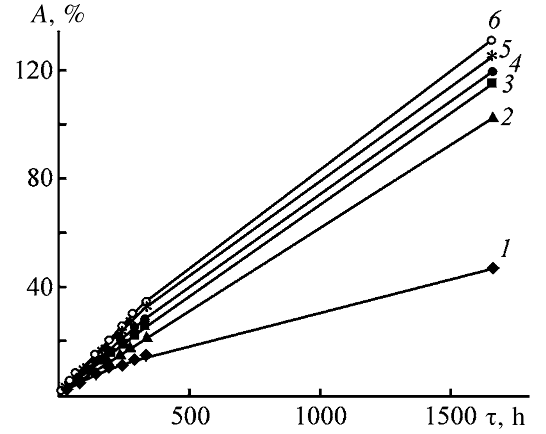

Fig. 10. Dynamic curves of water absorption *A* in a desiccator over water by (*1*) microcomplex, (*2*) ammonium sulfate, (*3*) ARVI microfertilizer, and (*4–6*) the same + 1, 3, and 4% AAC, respectively.

CONCLUSIONS

(1) Data obtained by instrumental methods show that no chemical reactions between the components occur in ARVI microfertilizer with additions of amino acid concentrate. The amino acid concentrate decreases the thermal stability of the fertilizers. Traditional conditions of granulation, drying, and storage are quite suitable for the fertilizers in question.

(2) Studies of water absorption under various conditions show that microelement fertilizers based on ammonium sulfate and containing amino acid concentrate do not change their physical properties.

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