

27. Gilleo, M. A. Ferromagnetic insulators: garnets. Vol. 2. Chap. 1 [Text] / M. A. Gilleo // Handbook of Ferromagnetic Materials. – North-Holland, 1980. – P. 1–53. doi: 10.1016/s1574-9304(05)80102-6
28. Ostafyichuk, B. K. Rozuporiadkuvannia struktury tverdykh rozchyniv lityi-zaliznoi ta lityi-aliuminyiovoi shpineli [Text] / B. K. Ostafyichuk, I. M. Hasiuk, V. V. Mokliak, B. Ya. Deputat, I. P. Yaremiy // Metallofizika i noveyshie tekhnologii. – 2010. – Vol. 32, Issue 2. – P. 209–224.
29. Lucas, A. V. Peculiar properties of crystal-chemical structure of spinels of the system  $Mg(Fe_xCr_{2-x})O_4$  obtained through the hydroxide coprecipitation method and solid state technology [Text] / A. V. Lucas, I. P. Yaremiy, M. P. Matkivskiy // Eastern-European Journal of Enterprise Technologies. – 2015. – Vol. 5, Issue 6 (77). – P. 57–63. doi: 10.15587/1729-4061.2015.51058

*Досліджено комплексоутворюючі властивості волокнистого комплексу на основі поліакрилонітрилу по відношенню до іонів міді(II) в сумішах вода-1,4-діоксан. Визначено константи стійкості комплексів міді(II) з гідроксамовими групами полімеру, стехіометричний склад отриманих комплексів. Встановлено вплив сольватаційних параметрів комплексу на процес комплексоутворення*

**Ключові слова:** модифіковане поліакрилонітрильне волокно, комплексоутворення, константи стійкості, розчинник вода-1,4-діоксан

*Исследованы комплексообразующие свойства волокнистого комплекса на основе полиакрилонитрила по отношению к ионам меди(II) в смесях вода-1,4-диоксан. Определены константы устойчивости комплексов меди(II) с гидроксамовыми группами полимера, стехиометрический состав полученных комплексов. Установлено влияние сольватационных параметров комплекса на процесс комплексообразования*

**Ключевые слова:** модифицированное полиакрилонитрильное волокно, комплексообразование, константы устойчивости, растворитель вода-1,4-диоксан

UDC 541.8

DOI: 10.15587/1729-4061.2017.110135

# RESEARCH INTO COMPLEXING PROPERTIES OF POLYACRYLONITRILE COMPLEXITE IN THE MIXTURES OF WATER-DIOXANE

**N. Korovnikova**

PhD, Associate Professor

Department of Fire and Technogenic Security of Facilities and Technologies

National University of Civil Protection of Ukraine  
Chernishevskaya str., 94, Kharkiv, Ukraine, 61023

E-mail: natalia.korovnikova@gmail.com

**A. Dubyna**

PhD, Associate Professor

Department of General Chemistry

V. Dokuchaev Kharkiv National Agrarian University  
Dokuchayev n/a "Communist-1",  
Kharkiv district., Kharkiv region, Ukraine, 62483

## 1. Introduction

Complexing fibers (complexites) are widely used in practice [1]. These polymeric materials have good kinetic, sorption, technical-operational characteristics. It is easy to produce filters, tapes, non-woven materials out of them, which are suitable for hardware implementation of technological processes.

Complexites selectively sorb metal ions from solutions and form with them high-molecular complex compounds (HMCC) of various stability [2]. Due to these properties, HMCC are used in catalysis, ionometry, for sorption-spectroscopic and test methods of analysis of the solid phase of ion exchange materials, and analytical chromatography. Thus, when designing technological modes of wastewater purification from heavy metal ions with the help of complex-

ing fibers-complexites, it is necessary to establish in advance optimal variants for fixing metal ions with polymers.

Special features of complexing processes involving polymeric ligands of the crosslinked structures are related to their cooperative nature [3]. Cooperative nature of complexites manifests itself in various interactions of functional groups in the polymer chain, its configuration and supramolecular changes, determining the conformation of matrix of a polymer and groups. In other words, in such systems, the primary balance, a heterogeneous chemical reaction of formation of supramolecular complex compounds between polymer groups and metal ions, is accompanied by the above-mentioned so-called "polymeric effects" [3]. The latter influence physical-chemical characteristics of HMCC and are the reason why their properties differ from analogous properties of low molecular complex compounds (LMCC) [2].

Such complexing reactions occur under complex heterogeneous conditions and are accompanied by mass transfer phenomena, protolytic, ion-exchange processes, different intra- and intermolecular interactions. When using polyfunctional complexites in non-aqueous or aqueous-organic mixtures, the range of related phenomena is expanding [2, 4]. That is why, when choosing optimal complexing conditions of complexite with metal ions, it is necessary to know thermodynamic, solvation, acid-basic properties of groups and reagents. Development of research in this direction is relevant, because by choosing a suitable solvent, it is possible to purposefully develop fiber-based materials with a pre-set complex of properties [4].

## 2. Literature review and problem statement

The problem of influence of a solvent on chemical equilibria of complexation is being intensively developed for low-molecular complex compounds [2, 5]. In the context of issues considered above, similar problems arise for polymers [3, 4]. In this case, participants of complexing reactions are polymeric ligands – fibers-complexites.

When studying the indicated processes in aqueous-organic solvents, in particular, in the mixtures of water-1,4-dioxane (water-DO), properties of a solvent significantly affect the equilibrium of complexation [2]. Authors of [6, 7], exploring sorption processes in the binary aqueous and non-aqueous solutions, drew a conclusion about essential impact of solvation by components of ion mixtures in the solution. Much to our regret, the scientific literature data on the solvating capability of individual ions in the mixtures water-1,4-dioxane are limited [5, 6, 8]. It is known that dioxane solvates cations better and has low solvating capability to anions [2, 8, 9].

HMCC are formed between metal ions and functional groups of a polymer in aqueous-organic mixtures. Thus, authors [10–12] studied processes of adsorption of copper(II) on the modified polyacrylonitrile nano-fiber by the method of atomic adsorption. Polyacrylonitrile modified fibers were investigated with a view to their practical application for selective sorption of ions of Cr(III) [13], Pd(II), Pt(IV) [14, 15]. In this case, the authors of [10–15] resolve issues related only to quantitative characteristics of sorption processes, without identifying mechanisms of the process, stoichiometry of resulting complexes.

Stability constants are quantitative characteristic of the resulting HMCC [5], similar to LMCC [2, 16]. Studies into stability of polymeric ligands of fibrous nature with metal ions in aqueous-organic solvents are rather limited [5, 17]. This is probably connected with experimental difficulties and interpretation of the data obtained.

The composition of macromolecular complexes [5] differs significantly from the composition of complexes of low-molecular analogues [2, 16]. According to authors of [5, 6], the structure and stability of HMCC, which fibrous complexites form with metal ions, are determined by many factors. These include the nature of functional groups, structure of polymer frame, the nature of metal of a complexing agent, effects of solvation – desolvation of reaction components. Formation of HMCC also significantly depends on flexibility of the polymer matrix and can alter with the change in the ratio of concentration of metal ions, ligand and pH values of the medium [4, 5, 16].

An analysis of the scientific literature [10–17] indicates the fact that the systems with polymer ligands in aqueous-organic solvents in the presence of transition metal ions are not studied sufficiently. It is expedient to examine the complexation processes in such complex systems based on the exploration of influence of a solvating factor on the reactivity of groups in polymers, and on their matrix.

## 3. The aim and objectives of the study

The aim of present research is to establish quantitatively characteristics of the complexation process and the composition of HMCC of copper(II) with the polyacrylonitrile complexite NAG considering solvation parameters of polymeric ligands in the mixed solvent water-1,4-dioxane.

To achieve the set aim, the following tasks had to be solved:

- to explore the equilibria of complexation of HMCC of copper(II) with the complexite NAG;
- to establish the influence of solvating parameters on the process of complexite with copper(II) ions in the mixed solvent water-1,4-dioxane.

## 4. Materials and methods of research into complexation process of the complexite NAG with copper(II) ions

### 4.1. Materials for research into complexing properties of fiber

The fibrous complexite NAG was received by chemical modification of the industrial fiber nitron [8]; its matrix contains functional groups of hydroxamic acid, amidoxime, and a small percentage of carboxyl groups. The polymer belongs to polyampholytes. The starting form of a polymer used in the experiments is mixed (hydrogen-hydrate-salt, H/OH, Cl): hydrogen by carboxylic, hydroxamic, oxyimino groups of amidoxime, and hydrogen-hydrate-salt – by amidoxime. Total exchange capacity (TEC, mmol/g) of the complexite was calculated from solutions of 0.1 M NaOH и 0.1 M HCl in water and mixtures. This magnitude characterizes the content of all types of functional groups in the fiber, the working exchange capacity ( $a_m$ , mmol/g) – the content of groups of specific type. Physical-chemical properties, ion exchange, solvation, protolytic, of the complexite NAG are described in [5].

The process of complexation of the complexite NAG with copper(II) ions was studied in a water-organic solvent. We used mixtures of water-DO at  $x=0.049, 0.17, \text{ and } 0.32$ . The mixtures were prepared by a gravimetric method, which provided accuracy of the compositions of mixed solvent at 0.02 %.

Quantitative characteristics of the complexing process include structure, stereochemistry, stability constants of NAG HMCC with ions of copper(II) (HMCC-  $\text{Cu}^{2+}$ ), constants of acid dissociation of NAG, calculated with and without taking into account solvation parameters. These data were compared with similar data for HMCC of copper(II) with a cellulose complexing fiber (the complexite CG [4, 18]) that contains the same functional groups.

The complexites NAG and CG vary by the nature of polymeric chains. The matrix of the former is a polyacrylonitrile fiber, the matrix of the latter is the grafted copolymer of cellulose and polyacrylonitrile. Properties of the objects, used in the present research, are described in [4, 5, 8, 18].

#### 4.2. Methods of research into equilibrium of complexation

To solve the task of present study, we applied methods of potentiometric titration, infrared spectroscopy, spectroscopy of diffuse reflection, and swelling.

Given the polyfunctionality of the complexite NAG, it is rather difficult to establish the structure of coordination centers of HMCC and places of localization of coordination bond in them. We shall solve this problem using the method of IR spectroscopy [19], comparing the spectra of the complexite and its complexes under the same conditions of experiment (solvent, pH of medium, temperature).

The IR spectra of samples of fibers, obtained in the contact of samples of complexite with aqueous and aqueous-dioxane solutions of copper(II) salts in the form of pills, were examined in the spectrophotometer Specord M80. Time of contact between batches of the complexite NAG, pH of the solutions, concentration of copper(II) salts met conditions for the potentiometric titration of fiber [8].

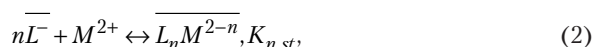
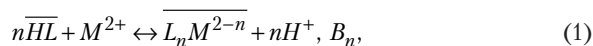
Potentiometric titration of the complexite, the complexite in the presence of copper(II) chloride, solution of copper(II) chloride, as well as the solution without all specified substances (idle experiment) was conducted in the mixtures water-DO in a pH range of 2.0–6.0 at  $I=0.1$  mol/l (NaCl),  $T=298.15$  K using the method described in [5]. A Solution of 0.1 M HCl was used as a titrant. To determine the time of establishing an equilibrium of the complexation reactions, we controlled pH values and the concentration of copper(II) ions in solutions after their contact with the complexite NAG. In these experiments, a change in the concentration of copper(II) ions in solutions was determined by a complexometric method [10] at regular intervals (24 hours, two, three, or more days). The time of establishing an equilibrium in the system depended on composition of the mixtures water-DO and increased with an increase in the dioxane concentration in water. These results coincide with similar data in the study into protolytic equilibria of the complexite NAG in the mixtures water-DO with a corresponding composition [8]. After the equilibrium was set, at each point of the curve of potentiometric titration, by complexometric method, we determined the equilibrium concentration of copper(II) ions in the solutions. Accuracy of measurement was  $\pm 1$  %.

All the obtained samples of NAG HMCC were colored, which allowed us to explore them using the spectra of diffuse reflection. The spectra were recorded by the spectrophotometer SP-46 in line with procedure described in [5, 20], taking into account the influence of particle dimensions, humidity and thickness of the layer of polymeric sample on spectral curves [5, 20]. Construction of diffuse reflection spectra was reduced to determining relative coefficients of diffuse reflection  $R_d$  at different wavelengths  $\lambda$ . The data were derived from the spectrophotometer with subsequent calculation of function  $F(R_d)$  at each  $\lambda$  by the Kubelka-Munch equation [21]. Thus, dependence  $F(R_d)=f(\lambda)$  is a diffuse reflection spectrum of the substance, close to the spectrum of its absorption in solution [5].

Solvation parameters in water and mixtures – swelling ( $m_1$ ,  $m_2$ ), specific volume ( $V_{sp}$ , ml/g) of a swollen polymer, were determined in the region of dissociation of groups in line with techniques described in [18]. The values of magnitudes  $m_1$  and  $m_2$  correspond to the content of DO and water in g/g of the air-dry sample of a polymer. Solvation parameters of NAG and HMCC-Cu<sup>2+</sup> (pH 2.0–6.0), spectral measurements (IR-spectra, diffuse reflection spectra),

as well as processing of experimental data, were carried out using techniques described in paper [5].

Complexation process is quantitatively described by constants ( $B_n$ ,  $K_{n,st}$ ), most often exploring the equilibria of reaction of substitution of proton of ligand groups with ion of metal ( $B_n$ ). Calculation of complexation constants ( $B_n$ ) and stability ( $K_{n,st}$ ) of HMCC was performed for the equilibria of type:



where  $\overline{HL}$  and  $\overline{L}$  are the protonated and deprotonated forms of ligand groups.

Next, the magnitude of stability constant was determined taking into account magnitudes of constants of their dissociation  $K_0$ :  $K_{n,st} = B_n/K_0$ .

Calculation of acid dissociation constants of groups taking into consideration solvation parameters was performed using the procedure described in [5]. The magnitudes of logarithms of stability constants of HMCC-Cu<sup>2+</sup> ( $\lg K_{st1}$ ) were calculated without taking into account solvation parameters. Values  $\lg K_{st1}^*$  were computed considering solvation parameters of the complexation process.

#### 5. Results of research into equilibria of complexation and properties of polymeric complexes

The original experimental data are the curves of potentiometric titration, or isotherms of metal ions sorption by a polymer [5, 18]. In both cases, it is necessary to have primary information on the concentrations of metal ion absorbed by the complexite, ligand groups associated with it, as well as pH values in the system at equilibrium.

Example of the curves of potentiometric titration of the complexite NAG in a mixture of  $x=0.32$  mol. d. DO is shown in Fig. 1.

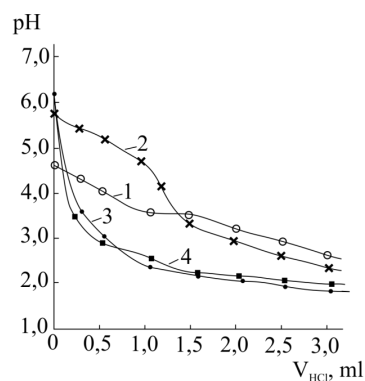


Fig. 1. Curves of potentiometric titration of the complexite NAG in the presence of copper(II) chloride solution in the mixture water-DO at  $x=0.32$ : 1 – complexite, 2 – complexite in the presence of solution of copper(II) salts, 3 – solution of copper(II) salt, 4 – “idle” experiment

Absorption bands in the spectra of diffuse reflection indicate the complexation of copper(II) ions with the complexite NAG (Fig. 3).

Obtained spectra of the diffuse reflection of the complexite NAG in mixtures (Fig. 3) are caused by  $d-d$  tran-

sitions, by the magnitude of exchange capacity of polymers for copper ions ( $g_m$ ) (Fig. 1). The latter is maximal in water, decreases in a mixture of  $x=0.049$ , changes little with an increase in the content of DO, but differs for metals similar by ions for HMCC CG [5] and HMCC-Cu<sup>2+</sup>.

Fig. 2 shows an example of the obtained IR-spectra, indicating the process of complexation of the complexite NAG with copper(II) ions.

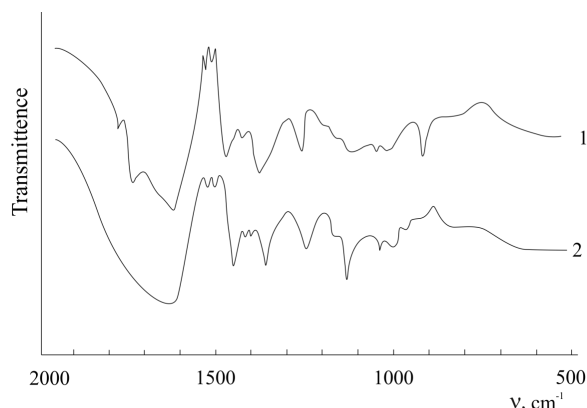


Fig. 2. IR-spectra of HMCC-Cu<sup>2+</sup> in water (pH 2.5–6.2) – (1), and in the mixture water-DO (pH 3.8–5.7) at  $x=0.32$  – (2)

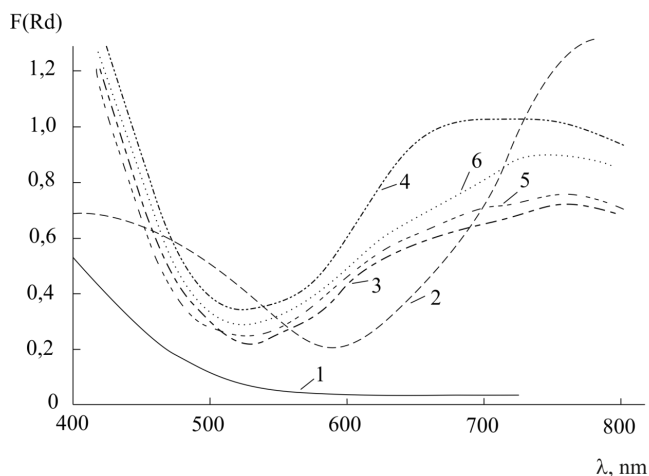


Fig. 3. Spectra of diffusion reflection of the complexite NAG – (1), CuCl<sub>2</sub>·2H<sub>2</sub>O – (2), complexes of HMCC-Cu<sup>2+</sup> – (3–6) at  $x$ : 0.0 – (3), 0.049 – (4), 0.17 – (5), 0.32 – (6)

For a quantitative description of equilibria in complexation and properties of the resulting polymer complexes, it is necessary to have information about stoichiometric composition, the structure of complexes, constants of reactions of their formation. The same data are also important for similar processes involving ligands of the low-molecular type [2, 16].

Information on the composition of coordination nodes of HMCC with copper(II) ions was also received from the values of  $n$  (Fig. 4). In mixtures for the complexes NAG, the magnitudes of  $\bar{n}$  are smaller than the values of  $n$ . In the range of pH 2.0–3.5, the values of  $n$  and  $\bar{n}$  are stabilized and testify to the formation of coordination centers in the complexites of stoichiometric composition M:L=1:1. Calculation of values for  $B_1$  in the equilibrium (1) in the specified systems (pH 2.0–3.5) was performed by employing, in accordance with the law of acting masses, experimentally

measured magnitudes of pH,  $g_m$ , [M<sup>2+</sup>], as well as calculated values [HL] [5].

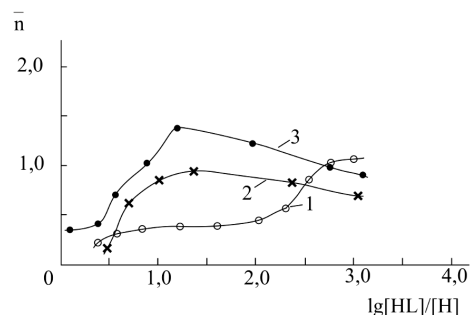


Fig. 4. Formation curves of  $\bar{n}=f(\lg[HL]/[H])$  of complexes of copper(II) with the complexite NAG, obtained without taking into consideration solvation parameters, in the mixtures water-dioxane at  $x$ : 0,0 – (1), 0,049 – (2), 0,17 – (3)

The calculation of constants was performed by the method of Bjerrum, modified by Gregor [5]. Obtained results are given in Table 1.

Table 1

Values of logarithms of stability constants of HMCC-Cu<sup>2+</sup> ( $\lg K_{st1}$ ,  $\lg K_{st1}^*$ ) and solvation parameters of the complexite NAG and HMCC-Cu<sup>2+</sup> – swelling ( $m_1$ ,  $m_2$ ), specific volume ( $V_{sp}$ , ml/g) in the mixtures water-1,4-dioxan at  $x=0.0$ –0.32 depending on dielectric permittivity  $\epsilon$  of the solution medium

$x$	100/ $\epsilon$	pH	Complexite NAG			HMCC-Cu <sup>2+</sup>			$\lg K_{st1}$	$\lg K_{st1}^*$
			$m_1$	$m_2$	$V_{sp}$	$m_1$	$m_2$	$V_{sp}$		
0.00	1.27	6.51–4.26	–	1.25	20.8	–	1.15	16.8	7.7	7.6
		3.83–2.11	–	1.75	22.1	–	1.32	18.7		
0.049	1.62	6.23–4.18	0.54	1.15	17.5	0.47	0.85	14.8	9.7	7.8
		4.00–2.14	0.62	1.25	19.4	0.43	0.75	16.5		
0.17	2.78	5.84–3.87	0.75	0.55	12.4	0.55	0.38	11.6	8.4	7.7
		3.76–2.10	0.92	0.42	18.6	0.62	0.26	14.3		
0.32	5.24	5.64–3.93	0.95	0.72	13.5	0.66	0.27	12.4	11.1	10.5
		3.61–2.00	1.55	0.54	27.8	0.79	0.22	21.5		

Data given in Table 1 indicate that solvation characteristics of the complexite NAG and HMCC-Cu<sup>2+</sup>, the values of logarithms of stability constants, calculated without considering ( $\lg K_{st1}$ ) and with consideration of solvation parameters ( $\lg K_{st1}^*$ ), depend on the nature of the mixed solvent water-DO, in which a complexation reaction occurs.

## 6. Discussion of results of research into complexing properties of the complexite NAG

When samples of the complexite NAG interact with copper(II) ions, the curves of potentiometric titration change as compared to the curves of titration of the complexite NAG itself. Example of the titration curves (Fig. 1) is given for a composition of the mixture water-DO at  $x=0.32$ . For the complexite NAG, the curves are located at lower pH (Curve 1), and during formation of NAG HMCC in the range of pH 3.8–6.2 ( $x=0.17$  and 0.32) their pH values become considerably higher (Curve 2). In this case, the swell-



ing of the complexite NAG in the presence of copper(II) ions depending on pH of the solution is significantly less compared to the swelling of samples of the complexite NAG [8].

In the spectra of HMCC-Cu<sup>2+</sup>, compared to the starting polymer NAG, new absorption bands appear, or there is a change in the position and contour of bands, responsible for valence and deformation oscillations of electron-donor groups (Fig. 2).

When copper(II) ions are introduced to the complexite NAG, in water and in composition of the mixture water-DO 0.049 m.d. DO, the IR-spectra of the samples demonstrate convergence and the blending of frequencies (1700–1600 and 1550 cm<sup>-1</sup>) occurs. In this case, an expanded band is formed (with a subsequent bathochromic shift) and the absorption intensity decreases until it disappears at 900–890 cm<sup>-1</sup>.

In the mixtures water-DO at  $x=0.17, 0.32$ , m.d., in the range of pH values 3.8–6.2, a new broad band appears at 900–850 cm<sup>-1</sup> due to the convergence of frequencies of 930 and 900–890 cm<sup>-1</sup> (amidoxime and hydroxamic groups).

A feature of the IR spectra of samples of HMCC-Cu<sup>2+</sup> in the mixtures water-DO is the existence of an absorption band of 1150–1130 cm<sup>-1</sup>, which is typical for the 1.4-dioxane cycle. This absorption band occurs due to the solvation of hydroxamic and protonated amidoxime groups of the complexite NAG by molecules of DO. Probably, as is the case for HMCC of the complexite CG [5], a specific solvation of the complexite matrix takes place here. The cause of specific solvation of the polymer matrix is formation of hydrogen bonds between molecules of DO and the fiber matrix, its functional groups. In this case, participation of DO molecules [5, 8] in the formation of coordination nodes of NAG HMCC is very likely.

Thus, the obtained results in a combination with similar data on model low molecular compounds [16] allow us to make an assumption about the mechanism of a complexation reaction. During interaction between the complexite NAG and copper(II) ions in the aqueous-dioxane mixtures, complexation proceeds with the participation of hydroxamic groups of the complexite in water and mixture at  $x=0.049$ , and in the mixtures at  $x=0.17$  and  $0.32$  – in the pH range of 2.2–3.8.

In the range of pH 3.8–6.2, along with hydroxamic groups, at  $x=0.17$  and  $0.32$ , amidoxime groups of the complexite are likely to take part in the formation of NAG HMCC. The features of spectra of the samples of HMCC-Cu<sup>2+</sup> (pH 3.8–6.2) do not allow us to draw a conclusion about stereochemistry of complexes in fiber.

Thus, spectral studies make it possible to assume that the absorption of copper(II) ions by a fibrous complexite occurs in line with the complexation mechanism. In this case, a nitrogen atom coordinates deprotonated amidoxime groups, oxygen coordinates C=O groups of hydroxamic acid, and the proton is split off.

Influence of solvation parameters on the complexation process in the examined system manifests itself when analyzing the magnitudes of swelling ( $m_1, m_2$ ), specific volumes ( $V_{sp}$ , ml/g) of the complexite NAG and HMCC-Cu<sup>2+</sup> in the mixtures of water-1.4 dioxane at  $x=0.0–0.32$  (Table 1). During transition from an aqueous system to the mixtures at  $x=0.049$ , the swelling of the complexite and HMCC-Cu<sup>2+</sup> decreases. For HMCC-Cu<sup>2+</sup>, values of  $V_{sp}$  are always lower than those of the complexite NAG. These data correlate with the values of magnitudes  $m_1$  and  $m_2$ , which correspond to the content of DO and water in polymer samples (Table 1).

The formation curves  $n=f(\lg[HL]/[H])$  of copper complexes (Fig. 4) are similar to the formation curves of HMCC

with polymeric ligands of the granular type [3]. The curves have a steep slope, which is typically associated with the cooperative nature of the process [3, 22]. For the complexite NAG, HMCC in the composition of 1:1 are formed in aqueous medium. In this case, attachment of metal ions takes place gradually and the shape of curves (they have a degree) is identical to that commonly observed for LMCC [2, 5, 15]. In other words, for NAG HMCC, coordination nodes  $M:L=1:1$  are formed in water. Under these conditions, the values of constants  $B_1$  were determined at  $\bar{n}=0.5$ . The formation curves of HMCC in the mixtures lack gradation, the curves have a steep slope, increasing with an increase in the content of DO, which indicates cooperativeness of the process. In this case, according to data from pH-metric titration in the pH range of 3.8–6.2, there forms a mixture of complexes of dominant composition  $\sim 1:1.5$  or  $\sim 1:2.5$  ( $x=0.17$  and  $0.32$ , amidoxime and hydroxamic groups), and at  $\text{pH} \leq 3.5$  – complexes that have a composition of  $M:L=1:1$  (hydroxamic groups). Considering the above data, the values  $K_{st}=B_1/K_0$  (the magnitudes  $K_0$  of hydroxamic groups of NAG [8]) were obtained for HMCC of the composition  $M:L=1:1$ .

Cooperativeness of the complexing process involving NAG manifests itself in the presence of DO ( $x=0.049$ ;  $M:L=1:1$ ). In the mixtures at  $x=0.17$  and  $0.32$ , the shape of the curves (Fig. 4) changes and the composition of complexes depends on the value of pH. Thus, in the range of pH 3.8–5.8, the magnitude of  $n$  increases, reaching the values of 2.0–2.5, then, at  $\text{pH} < 3.5$ , it sharply drops to unity, indicating stabilization of the HMCC composition at 1:1.

The changes observed seem to be linked to the transformation of the structure of coordination nodes that form at (pH 3.8–5.8) (type II) into coordination nodes created at pH 2.5–3.8 (type I). In this case, the former coordination nodes (type II), due to a larger content of metal ions in the polymer within the specified range of pH, will have a high positive charge. The charge is weakly shielded under conditions of predominant coordination of metal ion by the uncharged amidoxime groups. Then the resulting coordination nodes will be better solvated by the molecules of a non-aqueous solvent component. Probably for this reason, the swelling of NAG HMCC is large enough in the mixtures at  $x=0.17$  and  $0.32$  (Table 1).

The values of  $n$  and  $\bar{n}$  for NAG HMCC are significantly different. These facts are known and were discussed in a number of papers using chelation reactions with granular and fibrous complexites as an example [3, 22]. It was noted in [22] that a more reliable information is provided by magnitude  $n$  as a function of  $n$  reflects stoichiometry of the complex only at low concentrations of metal salt in a solution. Under these conditions, there are some excessive ligand groups relative to the metal bound to the complex. An acceptable concentration of salt was thought to be such at which the values of  $n$  and  $\bar{n}$  are close. However, authors of [22], in spite of the significant differences in the values of magnitudes  $n$  and  $\bar{n}$ , reported in the paper, applied a Bjerrum function of  $\bar{n}$  to calculate the constants of complexation.

Influence of the solvent manifests itself in a change, due to its introduction to the internal coordination sphere of the complex, in the composition of a complex compound. Thus, when participating in the reaction, the solvent is the same fully-fledged ligand as acids or bases [2]. Following this pattern, a change in the magnitudes of  $K_{st}$  of the complexes, in a transition from one solvent to another, or when changing a composition of the mixed solvent, should be determined by

the action of chemical and physical characteristics of the medium [2, 5]. In the case of research into protolytic equilibria of the complexite NAG, the same tendency is observed [18].

The effect of physical characteristic of the medium in a transition from one to another composition of the mixed water-aqueous solvent implies that the chemical process in the first approximation is reduced to electrostatic interactions. These interactions vary depending on the magnitude of dielectric permittivity of the solvent  $\epsilon$  (Turyan equation) [2, 5]). In the case of solvents, similar in chemical nature, there is a linear dependence of the type of magnitudes  $\lg K_{st}$  on  $1/\epsilon$ :  $\lg K_{st} = a + b/\epsilon$ .

It follows from the Irving and Rossotti equation [2] that  $\lg K_{st}$  is linearly dependent on the magnitude  $x$ , if the ratio of metal ion activity coefficients, ligand and a complex ion in water and mixed solvent is close to 1 or proportional to  $x$ . If a linear relationship  $\lg K_{st} = a + b/\epsilon$  is satisfied for any arbitrary system, then a straightness in the  $\lg K_{st} - x$  coordinates will hold if dependence  $1/\epsilon = f(x)$  is linear.

It follows from Table 1 that the magnitudes of stability constants of complexes  $\lg K_{st1}$ , calculated without taking into consideration solvation parameters, will grow in a transition from water to mixture at  $x=0.049$ , then their values decrease in the mixture at  $x=0.049$  and increase again at  $x=0.32$ . Such dramatic deviations from linearity prove a significant influence of the chemical factor on complexes' stability, which is determined by the effects of solvation by components of the mixed solvent. Solvation effects are associated with solvating capability of components of the mixed solvent water-DO relative to metal ions, ligand and complex compound [2]. Then, in the conditionally-universal, universal media, dependence  $\lg K_{st} = f(1/\epsilon)$  is linear and deviates from such in the systems dominated by specific solvation effects.

According to [2], extreme character of change in  $\lg K_{st}$  with an increase in the content of DO (Table 1) is caused by the structural features of mixtures ( $x=0.049$ ), over-solvation of particles ( $x=0.17$ ), restructuring of the coordination centers of HMCC by introducing to their coordination sphere of DO molecules (0.049, 0.32). In this case, a change in the magnitude  $e$  of the solvent does not noticeably affect the  $\lg K_{st}$  values, although the influence of the latter should not be entirely neglected ( $x=0.32$ ).

Authors of [2, 5, 8] argue that ions of transient metals, in the transition from water to the mixtures water-DO at  $x=0.049$ , are stabilized with their stability improved. The nature of change in the values of  $\lg K_{st}$  (Table 1) is likely due to the increased energy of solvation of metal ions and its differences from the complexite with increasing  $x$ . The com-

plexes, in which coordination of metal ions occurs through an oxygen atom, are typically characterized, following a decrease in the magnitude of  $e$ , by a sharp growth in the values of  $\lg K_{st}$ , which is actually observed in the water-organic solvent water=DO at  $x=0.32$ .

The obtained values of  $\lg K_{st1}^*$  for the resultant complexes HMCC-Cu<sup>2+</sup> differ from the values of  $\lg K_{st}$  (Table 1) and the character of dependence on  $1/\epsilon$ . Non-linearity of dependence  $\lg K_{st1}^*$  on  $1/\epsilon$  confirms significant influence of the solvation factor, which leads to the effects of particle over-solvation in mixtures. Solvation effects in the mixture water-1.4-dioxane with a molar fraction of DO at 0.00–0.17 reduce stability of the resulting complexes HMCC-Cu<sup>2+</sup>. The biggest effect of solvation parameters of the complexite is achieved in the composition of mixture at 0.32.

In such complex systems, by changing the composition of solvent in the mixtures with a wide range of dielectric permittivity ( $\epsilon$ ) of the medium, it is possible to control properties of a fibrous complexite. This information is particularly useful in the design of techniques for obtaining high-molecular complex compounds with the preset properties.

A higher stability of HMCC, compared to the aqueous medium, in the mixtures makes it possible to predict the possibility of applying complexites for purification of DO solutions from the impurities of d-transition elements.

## 7. Conclusions

1. When the complexite NAG interacts with copper(II) ions in the mixture water-1.4-dioxane, complexation occurs involving the hydroxamic groups of the polymer. In the range of pH 3.8–6.2, along with hydroxamic groups, in the mixtures with a molar share of dioxane at 0.17 and 0.32, the formation of HMCC-Cu<sup>2+</sup> involves amidoxime groups. The character of change in the stability constants of HMCC-Cu<sup>2+</sup> with an increase in the content of dioxane is due to the structural characteristics of mixtures, particle over-solvation, restructuring of the coordination centers of HMCC by introducing to their coordination sphere the DO molecules.

2. We established the effect of a solvation parameter on the composition and stability of the examined complexes with copper(II) ions. It was found that solvation effects in the mixture of water-1.4-dioxane with a molar share of dioxane at 0.00–0.17 reduce stability of the resulting complexes HMCC-Cu<sup>2+</sup>. The biggest impact of solvation parameters of the complexite is achieved in the composition of mixture at 0.32.

## References

1. Savvin, S. B. Sorbcionno-spektroskopicheskie i test-metody opredeleniya ionov metallov na tverdoj faze ionoobmennyh materialov [Text] / S. B. Savvin, V. P. Dedkova, O. P. Shvoeva // Uspekhi himii. – 2000. – Vol. 69, Issue 3. – P. 203–301.
2. Burger, K. Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents [Text] / K. Burger. – Elsevier Science, 1983. – 268 p.
3. Pomogaylo, A. D. Makromolekulyarnye metallohelaty [Text] / A. D. Pomogaylo, I. E. Uflyand. – Moscow: Himiya, 1991. – 304 p.
4. Miroshnik, L. V. The effect of background electrolyte on the physicochemical properties of a complex-forming cellulose fiber in water–dioxane mixtures [Text] / L. V. Miroshnik, N. I. Korovnikova // Russian Journal of Inorganic Chemistry. – 2002. – Vol. 47, Issue 8. – P. 1378–1385.
5. Miroshnik, L. V. Stability of copper(II) complexes with cellulose complexite in water-dioxane mixtures [Text] / L. V. Miroshnik, N. I. Korovnikova, Yu. V. Shabadash // Russian Journal of Inorganic Chemistry. – 2006. – Vol. 51, Issue 4. – P. 649–655. doi: 10.1134/s0036023606040255

6. Chen, G. Solubility and preferential solvation of econazole nitrate in binary solvent mixtures of methanol, ethanol and 1,4-dioxane in water [Text] / G. Chen, J. Chen, C. Cheng, Y. Cong, C. Du, H. Zhao // *The Journal of Chemical Thermodynamics*. – 2017. – Vol. 111. – P. 228–237. doi: 10.1016/j.jct.2017.03.038
7. Zhou, X. Adsorption of phthalic acid esters (PAEs) by amphiphilic polypropylene nonwoven from aqueous solution: The study of hydrophilic and hydrophobic microdomain [Text] / X. Zhou, J. Wei, H. Zhang, K. Liu, H. Wang // *Journal of Hazardous Materials*. – 2014. – Vol. 273. – P. 61–69. doi: 10.1016/j.jhazmat.2014.03.029
8. Miroshnik, L. V. Ion-exchange, solvation, and acid properties of complexing polyacrylonitrile fiber in water-dioxane mixtures [Text] / L. V. Miroshnik, N. I. Korovnikova // *Russian Journal of Applied Chemistry*. – 2000. – Vol. 73, Issue 1. – P. 44–50.
9. Madhurima, V. Wettability, FTIR and dielectric studies of 1,4-dioxane and water system [Text] / V. Madhurima, D. D. Purkayastha, N. V. S. Rao // *Journal of Colloid and Interface Science*. – 2011. – Vol. 357, Issue 1. – P. 229–233. doi: 10.1016/j.jcis.2011.01.090
10. Zhao, W. Preparation of Amino-Modified PAN Fibers with Triethylenetetramine as Aminating Reagents and Their Application in CO<sub>2</sub> Adsorption [Text] / W. Zhao, B. Liu, J. Chen // *Journal of Nanomaterials*. – 2014. – Vol. 2014. – P. 1–7. doi: 10.1155/2014/940908
11. Huang, F. Preparation of Amidoxime Polyacrylonitrile Chelating Nanofibers and Their Application for Adsorption of Metal Ions [Text] / F. Huang, Y. Xu, S. Liao, D. Yang, Y.-L. Hsieh, Q. Wei // *Materials*. – 2013. – Vol. 6, Issue 3. – P. 969–980. doi: 10.3390/ma6030969
12. Moghimi, A. Solid Phase Extraction of Trace Copper(II) Using Modified Nano Polyacrylonitrile Fiber [Text] / A. Moghimi, H. Mosalaj, H. Moghadam // *Journal of Chemical Health Risks*. – 2012. – Vol. 2, Issue 2. – P. 25–36.
13. Moghimi, A. Preconcentration of Cr(III) from Natural Water by Modified Nano Polyacrylonitrile Fiber by Methanolamine [Text] / A. Moghimi // *E-Journal of Chemistry*. – 2011. – Vol. 8, Issue 3. – P. 1052–1061. doi: 10.1155/2011/438735
14. Lim, A. Development of Surface-Modified Polyacrylonitrile Fibers and Their Selective Sorption Behavior of Precious Metals [Text] / A. Lim, M.-H. Song, C.-W. Cho, Y.-S. Yun // *Applied Sciences*. – 2016. – Vol. 6, Issue 12. – P. 378. doi: 10.3390/app6120378
15. Yoon, S. The Preparation of Modified Industrial Waste Polyacrylonitrile for the Adsorptive Recovery of Pt(IV) from Acidic Solutions [Text] / S. Yoon, S. Kim, C.-W. Cho, Y.-S. Yun // *Materials*. – 2016. – Vol. 9, Issue 12. – P. 988. doi: 10.3390/ma9120988
16. Agraval, I. K. Izuchenie gidroksamovyh kislot i ih metallokompleksov [Text] / I. K. Agraval // *Uspekhi himii*. – 1979. – Vol. 68, Issue 10. – P. 1773–1803.
17. Abovskii, N. D. Kinetics of platinum(II) and platinum(IV) sorption from hydrochloric acid solutions with a complexing ion exchanger containing thiourea functional groups and with a strongly basic anion exchanger [Text] / N. D. Abovskii, A. A. Blokhin, Yu. V. Murashkin // *Russian Journal of Applied Chemistry*. – 2007. – Vol. 80, Issue 7. – P. 1063–1067. doi: 10.1134/s1070427207070099
18. Miroshnik, L. V. The influence of cellulose complexite swelling on its protolytic properties in aqueous-organic mixtures [Text] / L. V. Miroshnik, N. I. Korovnikova, A. V. Aleksandrov, A. M. Dubyna // *Russian Journal of Physical Chemistry A*. – 2008. – Vol. 82, Issue 9. – P. 1484–1489. doi: 10.1134/s0036024408090148
19. *Introduction to Experimental Infrared Spectroscopy: Fundamentals and Practical Methods* [Text] / M. Tasumi (Ed.). – Wiley, 2014. – 408 p.
20. Ivanov, A. V. Reflectance spectra of organic matrices on the basis of photonic crystals formed of polystyrene microspheres with a particle size of 230 nm [Text] / A. V. Ivanov, A. A. Kozlov, A. N. Koreshkova, S. D. Abdullaev, I. A. Fedorova // *Moscow University Chemistry Bulletin*. – 2017. – Vol. 72, Issue 1. – P. 19–23. doi: 10.3103/s0027131417010060
21. Thennadil, S. N. Relationship between the Kubelka-Munk scattering and radiative transfer coefficients [Text] / S. N. Thennadil // *Journal of the Optical Society of America A*. – 2008. – Vol. 25, Issue 7. – P. 1480–1485. doi: 10.1364/josaa.25.001480
22. Ergozhin, E. E. Polifunkcional'nye ionoobmenniki [Text] / E. E. Ergozhin, E. Zh. Menligaziev. – Alma-Ata: Nauka, 1986. – 302 p.