

Досліджено комплексоутворюючі властивості волокнистого комплексу НАГ по відношенню до іонів нікелю(II) в змішаному розчиннику вода-1,4-діоксан. Спектральні дані свідчать, що поглинання волокнистим комплексом НАГ іонів нікелю(II) відбувається за механізмом комплексоутворення. Встановлено фактори, що впливають на комплексоутворення комплексу НАГ з іонами нікелю(II) в сумішах вода-1,4-діоксан, розраховано константи стійкості гідроксамових і амідоксимних груп в залежності від значень рН середовища та складу розчинника.

Встановлено вплив сольватаційного параметра на склад і стійкість досліджуваних комплексів НАГ з іонами нікелю(II). Сольватаційні характеристики комплексу НАГ і комплексів з іонами нікелю(II) залежать від природи змішаного розчинника, в якому відбувається реакція комплексоутворення. Сольватаційні ефекти в суміші вода-1,4-діоксан з мольною часткою діоксану 0,00–0,17 нівелюють стійкість комплексів, що утворюються.

Показано, що області значень рН 6,2–3,8 змішаного розчинника утворюються умови для існування ширшого за складом і будовою асортименту координаційних вузлів високомолекулярних комплексних сполук з різною часткою вмісту їх в полімері. Під час комплексоутворення тут беруть участь крім гідроксамових, і депротоновані амідоксимні групи. Крайня фіксація функціональних груп на поверхні волокна НАГ призводить до високої локальної концентрації реакційних центрів, підсилює кооперативність процесу, сприяючи легкій орієнтації груп при формуванні змішанолігандних координаційних вузлів високомолекулярних комплексних сполук. Оцінено константи стійкості депротонованих амідоксимних груп комплексу НАГ з іонами нікелю(II). Встановлено їхня залежність від складу розчинника

Ключові слова: поліакрилонітрильне волокно, комплексоутворення, сольватація, константи стійкості, вода-1,4-діоксан

FEATURES OF COMPLEX FORMATION OF A FIBROUS COMPLEXITE WITH NICKEL IONS IN WATER-DIOXANE MIXTURES

N. Korovnikova

PhD, Associate Professor*

E-mail: natalia.korovnikova@gmail.com

A. Dubyna

PhD, Associate Professor

Department of General Chemistry

Kharkiv National Agrarian University

named after V. V. Dokuchayev

township Dokuchaevsky, Kharkiv region,

Kharkiv district, Ukraine, 62483

V. Oliinik

PhD, Associate Professor*

E-mail: ptbot@ukr.net

*Department of Fire and Technogenic Security of Facilities and Technologies

National University of Civil Defence of Ukraine Chernyshevska str., 94, Kharkiv, Ukraine, 61023

1. Introduction

Complexing fibers (complexites) are widely used in practice in various technological processes to solve environmental problems associated with wastewater treatment processes of various industrial facilities [1]. Fibrous polymers are selective sorbents for extracting valuable (Pd and Pt) or removing harmful trace elements (Cu, Ni, Fe, Mo, V, Ti, and Bi) [2, 3].

When choosing one or another fibrous polymer, theoretical data are required for the complex of its properties, including dissociation constants and the structure of the resulting coordination unit of a high molecular complex compound (HMCC) [4]. For practical or research purposes, modified polyacrylonitrile-based polymers are often utilized [5]. The excellent sorption, kinetic properties [6] contribute to the widespread use of these substances in practice.

The functional groups of the fibrous complexer form stable HMCC with metal ions. The properties of HMCC depend on the type and ratio of groups in the polymer as

well as the nature of the solvent. Of particular importance is the quantitative measure of the stability of the resulting complexes – the stability constant of the functional groups of the complexer with a metal ion [4].

In the development of technological modes of applying fibre complexers, it is necessary to establish the best options for absorbing metal ions by the polymer. To do this, it is not enough to know only the sorption characteristics, since complexation proceeds under complex heterogeneous conditions, accompanied by mass transfer processes, protolytic, and ion exchange processes [7]. This spectrum expands with the use of complexites in organic mixtures in water [8].

Therefore, in such complex systems, along with thermodynamic parameters, it is essential to consider the influence of the solvation factor [6].

Given the widespread use of aqueous organic solvents in technological processes, it is important to study the features of complex formation processes and establish the influence of the solvent on the quantitative characteristics of complex formation in systems [10].

2. Literature review and problem statement

Despite the obvious practical importance of complexing fibers, the issues of controlling the properties of these substances remain poorly understood. In the study of such complex systems with the presence of a polyfunctional fibrous complexer and metal ions, or a mixed solvent, the important aspects are the influence of the solvent on the selectivity of the polymer and the activity of functional groups in the medium under study. An important issue is the ability to form stable complexes.

Thus, the results of a study of an effective sorbent based on polyacrylonitrile fibre to determine copper(II) ions are presented in [11]. In that case, the authors propose a method for concentrating and extracting the metal, based only on the sorption data of the modified fibre and do not address issues related to the complexation of the sorbent.

The same qualitative data are given in [12]. The authors explain the low sorption capacity of traditional sorbents based on polyacrylonitrile with respect to Pt(IV) ions by the insufficient ability of functional groups to bind. The interaction of a metal ion with functional groups of complexers leads to the formation of complexes. The reaction takes place in a heterogeneous environment, accompanied by the distribution of solvent molecules, metal ions and other components between the phases, protolytic and ion exchange processes. An equilibrium is established in the system, which is quantitatively described by constants. However, the authors do not carry out quantitative characteristics of complexation in the system. All tests are reduced to the construction of sorption isotherms. Probably, the lack of quantitative characteristics of complexation in the system under study is associated with objective difficulties in conducting the experiment.

Similar results are shown by the authors of [13]. Here, using Fourier transform infrared analysis (FT-IR) and scanning electron microscopy (SEM), the amidoximation reaction and the preparation of modified polyacrylonitrile fibre are confirmed. A surface-activated fibre, designated as a PAN-oxime fibre, was used to adsorb and extract Pd(II) and Pt(IV) ions. However, the authors of the work do not investigate the mechanism of the complexation of the functional groups and the composition of the resulting complexes. Because of the heterogeneity of functional groups and their mobility, due to the behaviour of the polymer matrix, coordination nodes of different composition arise. At the same time, the authors of [13] focus on the applied aspect of the results obtained with respect to these metal ions.

The data on the sorption of copper(II) and iron(III) ions on synthesized complexing nanofibres modified with hydroxylamine are given in [14]. Recommendations for the practical use of this fibrous sorbent are provided, based only on the sorption data.

The authors of [15] systematically investigated the adsorption properties, including the kinetics of adsorption, isotherms, and the effect of pH. The result shows that the amphiphilic structure and synergism between the hydrophilic and hydrophobic microdomains of the polymer can significantly improve the adsorption capacity, speed and affinity for adsorption of phthalic esters. However, there are also no quantitative characteristics and evidence of the processes under study.

It is noteworthy that the studies were conducted in aqueous media.

The complexity of studying these processes increases in the study of polymers in aqueous organic systems [5]. Thus,

it is shown in [9] that the role of a solvent with which it is possible to influence the selectivity of fibres in the formation of complexes with metal ions is essential. The conclusion about the predominant influence of solvation by the components of mixtures of ions in solution when studying sorption processes in binary aqueous and non-aqueous solutions was made by the authors of [16].

The structure and stability of the resulting HMCC are determined by the nature of the functional groups and the complexing metal, the complex polymer matrix, and the effects of solvation – that is, desolvation of the complex formation reaction components [9]. These characteristics can vary with changes in the ratio of concentrations of metal ions, ligand and pH values of the medium.

Thus, studying the stability of polymeric ligands of a fibrous nature with metal ions in aqueous-organic solvents is associated with experimental difficulties and interpretation of the data obtained, and such data are rather scarce.

Therefore, there is a reason to believe that research on the complexation of polyfunctional complexers in aqueous organic solvents should be carried out by studying not only their sorption properties. It is important to consider the entire range of quantitative characteristics of complexation in the system using various research methods. In this case, it is necessary to take into account the solvation factor, which can be controlled by changing the composition of the solvent in a wide range of dielectric constant values of the medium [9]. This necessitates research in the outlined direction.

3. The aim and objectives of the study

The aim of the study is to identify the characteristics of complex formation of a fibrous complexite NAG with a nickel(II) ion in a mixed solvent water-1,4-dioxane.

To achieve this aim, the following objectives were solved:

- to establish the factors affecting the complexation of the NAG complexite with nickel(II) ions in water-1,4-dioxane mixtures;
- to determine the influence of the solvation parameters on the complexation process of complexers with nickel(II) ions in a mixed solvent water-1,4-dioxane;
- to evaluate and establish the factors affecting the stability constants of the amidoxime groups participating in the complexation of the NAG complexite with nickel(II) ions in a mixed solvent.

4. Materials and methods for studying the features of the complexation process of the NAG complexite with nickel(II) ions

4.1. Materials for studying the complexing properties of the fibrous complexer

Samples of the NAG fibre complexite were used as objects of the study. Industrial Nitron was used as the matrix of the NAG fibre. The nitron fibre is a terpolymer of acrylonitrile, methyl methacrylate, and itaconic acid, and it contains ~92.5, ~6.0, ~1.5–2.0 % comonomer units, respectively [5]. Chemical modification of nitron was carried out with a hydroxylamine solution, varying the concentration, pH of the medium, and temperature [6]. The degree of conversion of nitrile groups in the modification process was controlled by the flow rate in the reaction of hydroxylamine, the concentration

of released ammonia, using the method of potentiometry, as well as according to elemental analysis (% of nitrogen) of the reaction products and their FEC. The maximum conversion of the nitrile groups to hydroxamic and amidoxime was achieved at an experimental temperature of 353.15 K, a pH of 6.9–7.1, and a hydroxylamine content of 36–40 g/l in solution. The amounts of hydroxylamine consumed during the modification and released ammonia, found by potentiometric titration, made it possible, in combination with the results of elemental analysis, to estimate the degree of conversion of nitrile groups to amidoxime, hydroxamic, and carboxyl. As a result of the modification of nitron, a NAG fibrous complexite was obtained, the characteristics of some samples of which are given in [5]. The physicochemical properties of ionexchange, solvation, and the protolytic complexer NAG are provided in [5, 6].

The complexation process of NAG complexers with nickel(II) ions was studied in an aqueous-organic solvent. As the medium, water-1,4-dioxane (DO) mixtures with a mole fraction of DO $x=0.049$, 0.17 and 0.32 were used. The mixture was prepared by a gravimetric method, which ensured the accuracy of the compositions of the mixed solvent of 0.02 %.

The quantitative characteristics of the complexation process are the composition, stereochemistry, stability constants of HMCC of functional groups of the NAG complexite with nickel(II) ions (HMCC–Ni²⁺) calculated without taking into account and with regard to solvation parameters.

4. 2. Methods for studying the complexing properties of the fibrous complexer

4. 2. 1. Methods for studying the features of the complexation process of the NAG complexite with nickel(II) ions

The study involved the methods of potentiometric titration, IR spectroscopy, diffuse reflection spectroscopy, as well as refractometric and pycnometric methods. The solvation characteristics were estimated by the values of swelling, specific volume, and the content of water-1,4-dioxane mixture components in the polymer and HMCC.

Potentiometric titration of the NAG complexite in water ($I=0.5$ mol/L) and in mixtures of the above composition ($I=0.1$ mol/L) was performed by the method of separate suspensions in the presence of nickel(II) chloride with a constant concentration in solution at a temperature of 298.15 K for the complexer maintaining the value of I with a NaCl solution. The weighed sample of the polymer was 0.1 g, the volume of the solution to be poured was 30 ml. Titration was conducted in neutral and acidic media, since nickel(II) hydroxides can be formed in the alkaline region. The titrant was a solution of HCl (0.1 mol/L) in water and mixtures. In parallel, under similar conditions, titration of the complexer was carried out in the absence of nickel(II), titration of solutions of metal salts in the absence of polymers, and titration of solutions in the absence of a metal salt and the complexer («blank» experiment). The equilibrium establishment time in the system depended on the composition of water-DO mixtures and increased with an increase in the concentration of DO in water. These results coincide with similar data in the study of the protolytic equilibria of the NAG complexer in mixtures of water-DO of the corresponding composition [6]. After equilibrium at each point of the potentiometric titration curve, the equilibrium concentration of nickel(II) ions in the solutions was determined by the complexometric method. The accuracy of determination was ± 1 %.

IR spectra of polymer complexes were recorded on a Specord M-80 spectrophotometer. For this purpose, HMCC samples were thoroughly ground in an agate mortar and pressed into tablets with KBr (1:30). Spectral studies were performed for HMCC obtained by contact of the complexer with aqueous and water-dioxane solutions of nickel(II) chloride. The contact time, the pH of the solution, the concentration of the nickel(II) salt corresponded to the conditions of potentiometric titration.

All the resulting HMCC were coloured, which made it possible to investigate them using diffuse reflectance spectra. The spectra were recorded on an SPH-18 spectrophotometer under the conditions described in [5]. Here, the relative diffuse reflection coefficients R_d were determined at different wavelengths λ . The data were obtained on the spectrophotometer with the subsequent calculation of the function $F(R_d)$ for each λ according to the Kubelka-Munk equation [17]. Thus, the dependence $F(R_d)=f(\lambda)$ is the diffuse reflection spectrum of a substance, and it is close to its absorption spectrum in the solution [4].

The complex formation process is quantitatively described by constants ($B_n, K_{n,stab.}$), investigating the equilibrium of the proton substitution reaction of the ligand groups by the metal ion (B_n). The calculation of the complexation constants of hydroxamic groups (B_n) and stability ($K_{n,stab.}$) of the HMCC was performed for the equilibria described [5]. The magnitudes of the logarithms of the stability constants of HMCC–Ni²⁺ ($\lg K_{stab.1}$) were calculated without taking into account the solvation parameters.

4. 2. 2. Methods for studying the effect of solvation parameters on the complexation process

Solvation parameters in water and mixtures – swelling (m_1, m_2) and specific volume ($V_{sp.}$, ml/g) of swollen samples of the complexer – were determined in the region of dissociation of groups by weight increment, volume of air-dry samples in equilibrium due to their absorption by the solvent described in [4]. The pycnometric measurement method described in [4] was used to calculate the specific volume ($V_{sp.}$).

The concentration of DO molecules in the initial mixtures and equilibrium solutions was determined refractometrically.

The calculation of acid dissociation constants of hydroxamic groups with regard to the solvation parameters was carried out according to the method described in [4]. The values $\lg K_{stab}^*$ were calculated taking into account the solvation parameters of the complexation process [5].

4. 3. 3. Methods for assessing the stability constants of amidoxime groups involved in complexation

The stability constants of the amidoxime groups of HMCC with nickel(II) ions were calculated in the pH range of 3.8–6.2. For this purpose, the values of $[H^+]$, HA_0 , HAc_0 , HA_0 , K_{0HA} , K_{0HL} , K_{0HAc} , as well as the values of the equilibrium concentrations of dissociated $[L^-]$, undissociated $[HL]$ hydroxamic, $[Ac^-]$, $[HAc]$ carboxyl groups, deprotonated $[A]$ and protonated $[HA^+]$ amidoxime forms. The calculation results show that in all cases the concentration of $[L^-]$ is low ($\sim 10^{-8}$ – 10^{-10}) and does not exceed the accuracy of determination. The concentration of $[HA^+]$ forms already in the initial portions of the potentiometric titration curves (pH 4.5–6.2) is high and increases with increasing acidity of the medium.

5. The results of studying the complexation process of the NAG complexite with nickel(II) ions in water-1,4-DO mixtures

5.1. The results of studying the features of the complexation process of the complexite with nickel(II) ions

An example of the curves of potentiometric titration of the NAG complexite in a mixture of $x=0.049$ mole fraction is shown in Fig. 1.

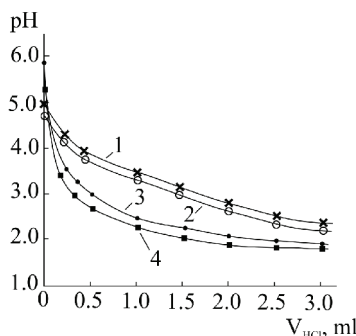


Fig. 1. The curves for potentiometric titration of the NAG complexite in the presence of nickel(II) chloride in a water-1,4-DO mixture with $x=0.049$: 1 – the complexite, 2 – the complexite in the presence of nickel(II) salt solution, 3 – nickel(II) salt solution, and 4 – «idle» experiment

The tests on the features of the equilibrium complexation of the NAG complexite with nickel(II) ions make it possible to establish IR spectroscopy data (Fig. 2). In this experiment, we used samples of the NAG complexite and HMCC with nickel(II) ions, obtained during potentiometric titration.

The stereochemistry of the resulting HMCC complexer is investigated by diffuse-reflective spectroscopy [5, 17]. As an example, Fig. 3 shows the diffuse reflectance spectra of the complexes of HMCC–Ni²⁺ at $x=0.17$ as well as the NAG complexite and the nickel salt NiCl₂·6H₂O.

Information on the composition of the focal points of the formed HMCC NAG with nickel(II) ions was also determined from the values of \bar{n} . The values of [H⁺], HL₀, K_{0HL}, K_{0HAc} were obtained from experimental tests, and the calculated concentrations of hydroxamic groups of the polymer formed the basis for determining auxiliary functions – the Bjerrum formation function \bar{n} [4, 5].

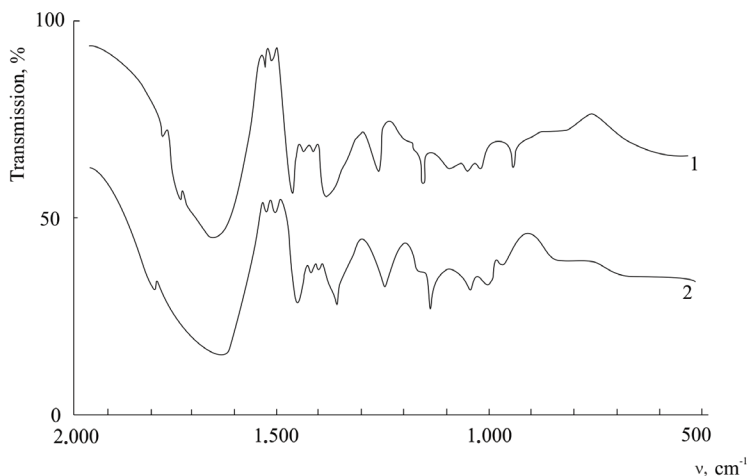


Fig. 2. IR spectra of HMCC–Ni²⁺ in water at pH 2.3–3.8 (1) and in the water-1,4-DO mixture with $x=0.17$ at pH 3.9–5.8 (2)

This value characterizes the average number of ligands per one metal ion. Table 1, as an example, shows the results of calculating the equilibrium concentrations of hydroxamic groups (mol/L) and the formation function \bar{n} for the Ni(II) system – the NAG complexite in a water-1,4-dioxane mixture (0.32 mole fraction of DO), $T=298.15$ K.

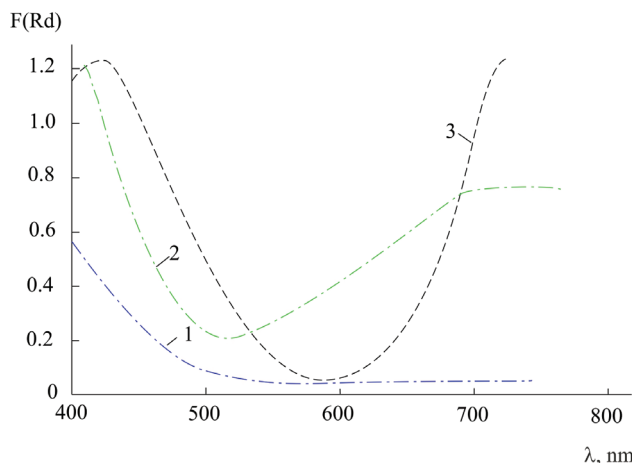


Fig. 3. Diffuse reflection spectra of the NAG complexite – (1), NiCl₂·6H₂O – (2), HMCC–Ni²⁺ – (3) at $x=0.17$

Table 1

The results of calculating the equilibrium concentrations of the groups (mol/L) and the formation function \bar{n} (0.32 mole fraction of DO)

C _{HCl} ·10 ³	pH	[M]·10 ³	[HL]·10 ³	lg $\frac{[HL]}{[H]}$	\bar{n}
0.00	5.70	1.8	3.99	3.30	3.56
1.66	5.13	1.8	1.65	2.34	5.47
3.33	4.70	1.9	3.31	2.22	4.11
5.00	3.39	1.9	4.95	1.05	3.06
6.66	2.90	1.9	5.40	0.63	2.40
8.33	2.60	2.0	5.81	0.36	2.06
10.00	2.40	2.0	6.11	0.19	1.83

As can be seen from Table 1, in the water-1,4-DO mixtures ($x=0.32$), the composition of the complexes depends on the pH value. In the pH range of 3.39–5.13, the value increases, reaching values of 3.06–5.47 and then dramatically decreases at pH<3.5. With a further decrease in the pH to one, the stabilization of a HMCC of 1:1 occurs.

5.2. The results of studying the effect of solvation parameters on the complexation process

The effect of solvation parameters on the complexation process is manifested in the analysis of swelling values (m_1 , m_2), specific volumes (V_{sp} , ml/g) of the NAG complexite and HMCC–Ni²⁺ in water-1,4-DO mixtures with $x=0.0–0.32$ (Table 2).

The value of V_{sp} was found taking into account the density of the samples in the sol-

vated state, measured by the pycnometric method using the method described in [4]. The total content of DO and water (m_1 and m_2 , respectively, in g/g of dry sample) absorbed by samples of polymers from the studied mixtures (pH 2.0–6.0) was determined by drying. The samples of NAG and HMCC were reduced to the constant weight for 5 hours.

Then, the concentration of DO in the initial mixtures, equilibrium solutions was determined refractometrically and, according to [4], the contents of the components of the water-dioxane mixture were calculated.

The calculation of the constants for the conditions of complexation of the polymer with nickel(II) ions was carried out by the Bjerrum method modified by Gregor [5] only for the NAG complexite system in water. In all systems in water-DO mixtures, the complex formation constants B_n were calculated according to the law of effective masses. In this case, we used the data of potentiometric curves of the NAG complexite in water-1,4-DO mixtures in the presence of the nickel(II) ion and material balance with respect to the hydrogen ion. The results are shown in Table 2.

The values of the logarithms of the stability constants and the solvation parameters of the NAG complexite and HMCC–Ni²⁺

X	100/ε	pH	NAG complexite			HMCC–Ni ²⁺			lgK _{stab.1}	lgK _{stab.}
			m ₁	m ₂	V _{sp.}	m ₁	m ₂	V _{sp.}		
0.00	1.27	6.50–4.02 3.70–2.10	–	1.15 1.56	20.1 22.0	–	1.10 1.22	15.4 17.2	6.6	6.5
0.049	1.62	6.21–4.00 4.11–2.15	0.53 0.57	1.10 1.11	18.1 18.9	0.37 0.33	0.81 0.74	14.6 15.1	9.0	8.8
0.17	2.78	5.80–3.77 3.75–2.12	0.72 0.88	0.45 0.40	13.3 16.6	0.45 0.52	0.33 0.22	12.6 13.3	8.5	8.4
0.32	5.24	5.60–3.40 3.69–2.11	0.95 1.35	0.66 0.49	12.5 21.0	0.60 0.72	0.23 0.20	12.2 17.1	10.6	10.3

Table 2 shows that the magnitudes of the logarithms of the stability constants of the hydroxamic groups of the HMCC–Ni²⁺ (lgK_{stab.1}, lgK_{stab.}) and the solvation parameters of the NAG complexite and HMCC–Ni²⁺ – swelling (m_1 , m_2) and specific volume ($V_{sp.}$, ml/g) depend on the composition of water-1,4-dioxane mixtures (the dielectric permittivity of the solution medium ε).

5.3. The results of calculating the stability constants of amidoxime groups involved in complexation

According to the data of [1] and of IR spectra, diffuse reflection spectra, a mixture of 1:2.5 complexes ($x=0.17$ and 0.32) is formed in the pH range of 3.8–6.2. Therefore, the stability constants of amidoxime groups, which also take part in the formation of HMCC–Ni²⁺, in pH ranges of 6.0–3.8, were calculated.

The results of calculating the stability constants of amidoxime groups of HMCC with nickel(II) ions are given in Table 3.

As can be seen from Table 3, the stability of the complexes formed by the deprotonated amidoxime groups of the NAG complexite with nickel(II) ions decreases with increasing DO in a mixed solvent.

Table 3

Values of the logarithms of the stability constants of the amidoxime groups of the HMCC–Ni²⁺ depending on the dielectric constant of the medium ε of the solution

x	100/ε	pH	lgK _{stab}
0.00	1.27	6.20–4.02	3.1
0.049	1.62	6.21–3.78	3.9
0.17	2.78	0.00–3.78	4.0
0.32	5.24	5.90–3.34	4.2

6. Discussion of the results of studying the complex-forming properties of the NAG complexite with nickel(II) ions in water-1,4-DO mixtures

Curves of potentiometric titration (Fig. 1) provide primary information on the concentrations of nickel(II) ions sorbed by the NAG complexite, the ligand groups associated with it, and also on the pH values in the system at equilibrium. The experimental titration curves were obtained by the method of individual weights for all the studied systems of the NAG complexite in the presence of a solution of nickel(II) chloride in a water-1,4-DO mixture. The obtained samples were used for spectral tests.

The IR spectra of the samples (Fig. 2) indicate the complexation of the NAG complexite with nickel(II) ions. Compared to the initial polymers, new absorption bands appear in the spectra of the formed HMCC, or the position and contour of the bands responsible for stretching and deformation vibrations of the electron-donating groups change. In water-1,4-DO mixtures, the spectra of the NAG complexite samples [4, 5] are similar to spectra for water systems [5].

The differences between the forms, as in water, appear in the frequency range of 1580 cm⁻¹, the intensity and position of which depend on the degree of dissociation of the hydroxamic and carboxyl groups of the fibre.

Changes in the HMCC spectra of the NAG complexite in water and mixtures of $x=0.049$ occur in the same frequency ranges as in the CH groups [4]. Here, the intensity of the 1,700–1,600 cm⁻¹ band decreases, which approaches the absorption frequency of 1,580 cm⁻¹, and the band at 1,700–1,500 cm⁻¹ appears broader than of the HMCC CG [4]. Apparently, under these conditions, taking into account changes in the range of 900–890 cm⁻¹, similar to those of the HMCC CG [4], the interaction of metal ions also occurs with donor oxygen atoms of the hydroxamic groups of the complex. The differences in the IR spectra of the complexes obtained in mixtures with $x=0.17$ and 0.32 are determined by the initial form of the polymer. This refers to the spectral characteristics of HMCC formed at pH 3.8–6.2 (the initial form of the polymer is mixed) and 2.2–3.8 (the original form is protonated). The spectra of the HMCC based on the protonated form of the NAG complexite are identical to the spectra of the CG [4] and NAG complexites in water and a mixture of $x=0.049$, and for the mixed one they coincide with the spectra of all the above

complexes only in the absorption regions of 1,700–1,600 and 1,580 cm^{-1} . Differences are observed for frequencies of 930 and 900–890 cm^{-1} . Here the convergence and imposition of these bands occur with the formation of a broadened band at 900–850 cm^{-1} , shifted to the low-frequency range, or their complete disappearance. The spectral tests suggest that when complexing the NAG complexite with nickel(II) ions, the nitrogen atom coordinates the deprotonated amidoxime groups, the oxygen coordinates the C=O group of the hydroxamic acid, and the proton is cleaved.

Thus, the spectral data suggest the joint participation in the formation of a coordination bond with metal ions of the hydroxamic and deprotonated amidoxime groups of the NAG complexite for HMCC obtained at pH 3.8–6.2. Moreover, the proportion of amidoxime groups that have entered into complexation will, according to [5], depend on their degree of protonation. A common feature of the spectra of all HMCC in mixtures is the presence of an absorption band of 1,150–1,130 cm^{-1} [4], indicating the participation of DO molecules in the formation of the HMCC.

The complexation of nickel(II) ions with the NAG complexite is indicated by absorption bands in the diffuse reflectance spectra. The most informative are absorption bands caused by $d-d$ -transitions directly associated with the spatial and electronic structure of the complexes [7]. They are observed in the spectra of all the studied HMCC obtained in water and mixtures in the pH range of 2.2–6.2. We do not have sufficiently complete (consistent) spectral characteristics of the complexes Cu(II), Co(II), and Ni(II) with hydroxamic acids and amidoximes. Therefore, to interpret the spectra of the HMCC, only those of them were used where the composition of the LMCC corresponds to $M:L=1:1$ [18]. The spectra of polymer complexes and solid metal salts were also compared. The spectra of HMCC NAG with Cu(II) ions [5] and Ni(II) for aqueous systems are identical to the spectra of similar complexes of CG [4], which indicates the similarity of their configurations.

The diffuse reflectance spectra of HMCC NAG–Ni²⁺ for aqueous systems are identical to the spectra of similar complexes of CG [4], which indicates the similarity of their configurations. The experimental data of diffuse reflectance spectra of NAG and HMCC–Ni²⁺ samples obtained in aqueous solutions (pH 2.2–6.2) indicate the introduction of the nickel ion, water molecules, and hydroxamic groups of the polymer into the coordination sphere. At the same time, the octahedral square-plane configuration [4] is established for the HMCC Cu(II), and two types of coexistence are possible in Ni(II) – the octahedral and tetrahedral structures [10].

The spectra of HMCC Ni(II) with the NAG complexite (pH 2.2–3.8), as in the copper complexes [4, 5], are identical. Most of the copper complexes, including those with hydroxamic acids, due to their special electronic configuration, as compared to the Ni(II) complexes, have a distortion of the octahedral and square structures [19].

The diffuse reflectance spectra of NAG complexite in mixtures are due to the $d-d$ -transitions and the exchange capacity of polymers for nickel(II) ions. The spectra of NAG complexite (pH 3.8–6.2) differ from those discussed above (pH 2.2–3.8) by a higher intensity and a wider general contour of the maximum of the $d-d$ -transitions corresponding to absorption areas of 650–760 nm. The peculiarities of the spectra of HMCC NAG (pH 3.8–6.2) do not allow making a conclusion about the stereochemistry of the complexes in the fibre. For NAG complexes with Ni(II) ions, complex interconversions of the octahedral, tetrahedral, and square

structures are possible, making it difficult to identify them under the conditions of the polymer chain. It is known that with hydroxamic acids, Ni(II) forms complexes of octahedral and tetrahedral structures [18].

In the NAG complex, the 1:1 composition of the HMCC is formed in an aqueous medium [5]. In this case, as in the complexes of Cu(II) with CG, [4], the addition of metal ions occurs gradually, which is identical to the behaviour of low molecular weight compounds (LMCC) [18].

The cooperative nature of the complexation process with the participation of NAG is manifested in the presence of DO ($x=0.049$; $M:L=1:1$), and in mixtures with $x=0.17$ and 0.32 (Table 1), the composition of the complexes depends on the pH value. Thus, in the pH range of 3.8–5.8, the value increases, reaching values of 2.0–2.5, then decreases sharply at pH<3.5, indicating stabilization of the HMCC of 1:1. Table 1 shows that with decreasing pH, the values of \bar{n} initially increase but then fall. Similar changes in the values were established in other compositions of water-1,4-DO mixtures. Apparently, in the range of pH values of 6.2–3.8, conditions are formed for the formation of a wider range of composition and structure of the range of HMCC co-ordination units with different proportions of their content in the polymer. It is likely that, in addition to the hydroxamic, deprotonated amidoxime groups also participate in the complexation.

The preferred fixation of groups on the surface of the NAG fibre and its lower swelling as compared with CG [4] lead to a high local concentration of the reaction centres. This circumstance enhances the cooperativeness of the process, facilitating easy orientation of the groups during the formation of mixed-ligand coordination nodes of the HMCC.

During the transition from the water system to the mixtures with $x=0.049$, the swelling capacity of the complex and HMCC–Ni²⁺ decreases. For HMCC–Ni²⁺, the V_{sp} values are always less than for the NAG complexite. These data correlate with the values of m_1 and m_2 , which correspond to the content of DO and water in the polymer samples (Table 2).

The change in the stability constants of the complexes with increasing x in the mixtures (Table 2) is attributed to the effect of the values, the structure of the solvent, the effects of the rearrangement of the coordination sphere of metal ions, and the solvation characteristics of the particles [5, 10]. In this case, resolution occurs during the transition from one composition of one mixture to another, and there is the dilution factor [8], the role of which may be far from minor.

From Table 2 it follows that the values of $\lg K_{stab.}$ of HMCC–Ni²⁺ is greater in mixtures than in water, and changes in the values of $\lg K_{stab.}$ from 1/e have extreme character. The values of the logarithms of the stability constants, calculated without taking into account ($\lg K_{stab.}$) and taking into account the solvation parameters ($\lg K_{stab.1}$), the solvation characteristics of the NAG complexite and HMCC–Ni²⁺ depend on the nature of the mixed solvent.

Another confirmation of the solvation effect is the absence of a clear sequence of changes with a decrease in ϵ of the pK_0 values of the CG complexite and $K_{stab.}$ of the HMCC. It concerns the indicated values for different mixed media (water–DO as well as previously studied water–methanol and water–dimethyl sulfoxide in [10]). Thus, for example, a water-1,4-DO mixture ($x=0.32$), which has a low value of $\epsilon=19.07$, has approximately the same stabilizing effect on the stability of HMCC with a water–methanol mixture ($x=0.83$) although the value of ϵ of the latter is significantly higher ($\epsilon=37.9$). At the same time, with fairly close ϵ mix-

tures of water-methanol ($x=0.83$, $\epsilon=37.9$) and water-1,4-DO ($x=0.17$, $\epsilon=35.85$), the K_{stab} values of the HMCC in them differ by about 1.5–2.0 orders of magnitude. Similar patterns have been established for low molecular weight systems [8]. This may be evidence of a noticeable effect of the solvation of the polymeric ligand on the stability of the HMCC.

The influence of the solvation parameter in the systems studied shows the results that are presented in Table 2. As can be seen, the values of $\lg K_{stab}^*$ increase with the transition from water to mixtures, as in the case of $\lg K_{stab}$, but their values are smaller. The solvation effects in the water-1,4-dioxane mixture with an increase in the molar fraction of dioxane of 0.00–0.17 level off the stability of the resulting HMCC–Ni²⁺ complexes.

Fig. 3 shows the $\lg K_{stab}$ data for the formation of HMCC–Ni²⁺ complexes, assuming that only amidoxime groups are involved in the complexation process in the presence of deprotonated amidoxime groups (pH 3.8–6.2). The values of $\lg K_{stab}$ increase with increasing the molar fraction of DO in the mixed solvent. These ideas are consistent with the data of [19] that low-molecular amidoximes in the above pH range form stable complex compounds with *d*-transition metals. The carboxyl groups of the NAG complexite already at pH ≤ 4.5 are practically not dissociated, and the values of [NAC] are constant and close to their initial concentration (NAC₀) in the polymer. At the same time, a decrease in pH values leads to a gradual involvement of the hydroxamic groups of the polymer in the complexation process.

The qualitative interpretation of the data could be more correct in the presence of information on the transfer functions of the proton, metal ions and ionic forms of polymers. For this and a number of other reasons, it is not possible to

estimate the contribution of solvation of polymers to the complexation process, although its effect is obvious. The same tendency takes place in the HMCC CG in water-methanol mixtures [10]. Therefore, the solvation contribution can be quite significant and the study of the possibility of its evaluation is advisable.

7. Conclusion

1. The properties of the formed stable high-molecular complex compounds of the complexes in the interaction of the NAG complexite with nickel(II) ions in a water-1,4-dioxane mixture depend on the nature of the solvent as well as the type and ratio of groups in the polymer depending on the pH of the medium. The cooperative nature of the complexation process with the participation of NAG is manifested in a water-1,4-dioxane mixture with a molar fraction of dioxane of 0.049. In mixtures with a molar fraction of dioxane of 0.17 and 0.32, the composition of the complexes depends on the pH value.

2. The effect of the solvation parameter on the composition and stability of NAG complexes with nickel(II) ions has been established. The solvation effects in a water-1,4-dioxane mixture with a molar fraction of dioxane of 0.00–0.17 level off the stability of the resulting HMCC–Ni²⁺ complexes.

3. The stability constants of the deprotonated amidoxime groups of the NAG complexite with nickel(II) ions are estimated in a wide dielectric constant range of the mixed water-dioxane solvent. Their dependence on the composition of the water-1,4-dioxane mixture has been established. The values of $\lg K_{stab}$ increase with increasing molar fraction of dioxane in the mixed solvent of water-1,4-dioxane.

References

- Saldadze K. M., Kopylova-Valova V. D. Kompleksoobrazuyushchie ionity (kompleksity). Moscow: Himiya, 1980. 336 p.
- Iqbal M., Saeed A., Zafar S. I. Hybrid biosorbent: An innovative matrix to enhance the biosorption of Cd(II) from aqueous solution // *Journal of Hazardous Materials*. 2007. Vol. 148, Issue 1-2. P. 47–55. doi: <https://doi.org/10.1016/j.jhazmat.2007.02.009>
- Design of High Efficiency Chelate Fibers with an Amine Group To Remove Heavy Metal Ions and pH-Related FT-IR Analysis / Shin D. H., Ko Y. G., Choi U. S., Kim W. N. // *Industrial & Engineering Chemistry Research*. 2004. Vol. 43, Issue 9. P. 2060–2066. doi: <https://doi.org/10.1021/ie030696f>
- Miroshnik L. V., Korovnikova N. I., Shabadash Y. V. Stability of copper(II) complexes with cellulose complexite in water-dioxane mixtures // *Russian Journal of Inorganic Chemistry*. 2006. Vol. 51, Issue 4. P. 649–655. doi: <https://doi.org/10.1134/s0036023606040255>
- Korovnikova N., Dubyna O. Research into complexing properties of polyacrylonitrile complexite in the mixtures of water-dioxane // *Eastern-European Journal of Enterprise Technologies*. 2017. Vol. 5, Issue 6 (89). P. 63–69. doi: <https://doi.org/10.15587/1729-4061.2017.110135>
- Miroshnik L. V., Korovnikova N. I. Ion-exchange, solvation, and acid properties of complexing polyacrylonitrile fiber in water-dioxane mixtures // *Russian Journal of Applied Chemistry*. 2000. Vol. 73, Issue 1. P. 44–50.
- Pomogaylo A. D., Uflyand I. E. Makromolekulyarnye metallohelaty. Moscow: Himiya, 1991. 304 p.
- Burger K. Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents. Akademia Kiado, 1983. 256 p.
- The influence of cellulose complexite swelling on its protolytic properties in aqueous-organic mixtures / Miroshnik L. V., Korovnikova N. I., Aleksandrov A. V., Dubyna A. M. // *Russian Journal of Physical Chemistry A*. 2008. Vol. 82, Issue 9. P. 1484–1489. doi: <https://doi.org/10.1134/s0036024408090148>
- Miroshnik L. V. The peculiarities of high-molecular complex compounds of metal ions with fibrous complexites in water-organic mixtures // *Journal of Molecular Liquids*. 2001. Vol. 91, Issue 1-3. P. 245–253. doi: [https://doi.org/10.1016/s0167-7322\(01\)00169-6](https://doi.org/10.1016/s0167-7322(01)00169-6)
- Moghami A., Mosalayi H., Moghadam H. Solid Phase Extraction of Trace Copper(II) Using Modified Nano Polyacrylonitrile Fiber // *Journal of Chemical Health Risks*. 2012. Vol. 2, Issue 2. P. 25–36.
- The Preparation of Modified Industrial Waste Polyacrylonitrile for the Adsorptive Recovery of Pt(IV) from Acidic Solutions / Yoon S., Kim S., Cho C.-W., Yun Y.-S. // *Materials*. 2016. Vol. 9, Issue 12. P. 988. doi: <https://doi.org/10.3390/ma9120988>
- Development of Surface-Modified Polyacrylonitrile Fibers and Their Selective Sorption Behavior of Precious Metals / Lim A., Song M.-H., Cho C.-W., Yun Y.-S. // *Applied Sciences*. 2016. Vol. 6, Issue 12. P. 378. doi: <https://doi.org/10.3390/app6120378>

14. Preparation of Amidoxime Polyacrylonitrile Chelating Nanofibers and Their Application for Adsorption of Metal Ions / Huang F, Xu Y, Liao S, Yang D., Hsieh Y.-L., Wei Q. // Materials. 2013. Vol. 6, Issue 3. P. 969–980. doi: <https://doi.org/10.3390/ma6030969>
15. Adsorption of phthalic acid esters (PAEs) by amphiphilic polypropylene nonwoven from aqueous solution: The study of hydrophilic and hydrophobic microdomain / Zhou X., Wei J., Zhang H., Liu K., Wang H. // Journal of Hazardous Materials. 2014. Vol. 273. P. 61–69. doi: <https://doi.org/10.1016/j.jhazmat.2014.03.029>
16. Zhao W., Liu B., Chen J. Preparation of Amino-Modified PAN Fibers with Triethylenetetramine as Aminating Reagents and Their Application in CO₂ Adsorption // Journal of Nanomaterials. 2014. Vol. 2014. P. 1–7. doi: <https://doi.org/10.1155/2014/940908>
17. Thennadil S. N. Relationship between the Kubelka-Munk scattering and radiative transfer coefficients // Journal of the Optical Society of America A. 2008. Vol. 25, Issue 7. P. 1480. doi: <https://doi.org/10.1364/josaa.25.001480>
18. Pilipenko A. T., Zul'figarov O. S. Gidroksamovye kisloty. Moscow: Nauka, 1989. 312 p.
19. Yuferova I. B., Fadeeva V. I., Tihomirova T. I. Kompleksoobrazovanie medi(II) s alkilamidoksimom v vodnom rastvore i v faze kremnezemnogo sorbenta // Zhurn. neorg. himii. 1989. Vol. 34, Issue 2. P. 361–365.

Дослідження проводили з використанням потріпної інтумесцентної системи, яка базується на Exolit AP 740 F і представляє собою синергетичний систему на основі поліфосфатів амонію з додаванням азот-вмісних сполук. В якості зв'язуючого використовувався стирол-акриловий полімер, роль пігменту виконував діоксид титану. Пластифікатори в дослідженні були обрані таким чином, щоб оцінити вплив їх молекулярної маси на структуру піни. В якості пластифікаторів були обрані: дибутилфталат і полібутенові олігомери: Indopol H 1200, Indopol H 6000 і Indopol H 18000.

Результати представлені у вигляді зображень електронної мікроскопії, часу досягнення критичних температур при випробуванні пальником Бунзена, коефіцієнти спучування композиції, а також графіків термогравіметричного аналізу.

Встановлено вплив пластифікаторів на пористу структуру і вогнестійкість вуглецевих піни інтумесцентних покриттів. На прикладі полібутенових алифатичних матеріалів були визначені температурні інтервали термоокислювальної деструкції пластифікаторів, встановлена залежність їх стабільності при термічній обробці від значення молекулярної маси. Показано, що застосування пластифікаторів різної молекулярної маси дозволяє змінювати розміри комірок піни, шляхом зниження показника границі текучості розплаву, що призводить до збільшення розмірів цих комірок. При збільшенні молекулярної маси здатність пластифікатора формувати асоціативні структури зростає, що підвищує межу текучості розплаву і знижує значення середнього діаметра комірки піни, а також змінювати характер утворення контракційних трищин в структурі. Встановлено, що показник вогнестійкості покриттів залежить від типу і молекулярної маси використовуваних пластифікаторів. Для розглянутої інтумесцентної системи на основі стирол-акрилового полімеру виявлена залежність вогнестійкості від молекулярної маси пластифікатора.

Результати дослідження можуть бути використані при розробці рецептур інтумесцентних систем для протипожежного захисту

Ключові слова: інтумесцентне покриття, вуглецева піна, пластифікатор, термоізоляція, структура вуглецевого шару, вогнезахист

UDC 667.637.232.2, 661.174

DOI: 10.15587/1729-4061.2019.162554

INFLUENCE OF PLASTICIZERS ON FIRE RETARDING PROPERTIES OF CARBON FOAMS OF INTUMESCENT COATINGS

O. Myronyuk

PhD, Associate Professor*

E-mail: whizershines@gmail.com

D. Baklan*

E-mail: denisbaklan1kpi@gmail.com

S. Barrat

PhD, Professor

Materials department,

Institut Jean Lamour,

Courbet, 37, Maxeville, France, 54320

E-mail: silvere.barrat@univ-lorraine.fr

S. Yezhov

Postgraduate student*

E-mail: Sergii.ezhov@gmail.com

V. Svidersky

Doctor of Technical Sciences, Professor*

E-mail: xtkm@kpi.ua

*Department of Chemical Technology of Composition Materials

National Technical University of Ukraine

«Igor Sikorsky Kyiv Polytechnic Institute»

Peremohy ave., 37, Kyiv, Ukraine, 03056

1. Introduction

Intumescent coatings are a relatively new, but at the same time a very extensive class of materials used as passive

fire protection. In 2017, their market volume amounted to about USD 900 million, every year the market is growing by 4–6 % on average [1]. The basic principle of operation of this protection is formation of porous coal foam when covering