Petroleum and Coal

Article **Open Access**

Investigation the Process Interaction of the Copper Ions (II) with Polyacryl Acid

Lilianna Oliynyk, Makota Oksana, Nataliya Bernatska, Zoryana Komarenska

Lviv National Polytechnic University, 12, Bandera str., 79013 Lviv, Ukraine

Received March 18, 2021; Accepted August 9, 2021

Abstract

The process of interaction of copper ions with polyacrylic acid is investigated in this paper. It is shown that complexes are formed by the interaction of polyacrylic acid with copper ions (II) in a wide range of pH. At pH < 4, the precipitate of complexes falls, the pH of the solution increases, water-soluble copper complexes (II) with polyacrylic acid are formed. The solubility of such complexes depends on the number of ionized carboxyl groups of the macromolecule. At low concentrations of copper ions (II) in the mixture, complexes associated with two carboxyl groups of polyacids are formed. At high concentrations of copper ions (II), one ion of copper(II) binds only one carboxyl group, and hydroxocomplex copper(II) is formed. It was established that the viscosity of aqueous solutions of polyacrylic acid decreases with an increase in the concentration of copper ions (II) due to the formation of complexes between them. The influence of the pH of the solution, the concentration of polyacrylic acid, and copper ions (II) in the solution on the amount of bound copper during the formation of copper salt sediment with polyacids is shown. The process of dehydration of copper(II) complexes with polyacrylic acid were studied.

Keywords: *Complexes; Polyacrylic acid; Polyacids; Copper ions (II); Carboxyl-containing polymers.*

1. Introduction

Carboxyl-containing polymers, in particular polyacrylic acid, are used in water purification [1-2], separation of heavy metal salts [3-4], and in other cases. Therefore, the study of the interaction of metal ions, as well as their complexes with polymers and polymeric acids in aqueous solutions continues [5-6]. Polymers with functional groups are used for the production of metal particles and their oxides with definite sizes in the form of stable aqueous dispersions [7-9]. The stability of such dispersions depends on the strength of the bond between the surface of the particle and the polymer and on the hydrophilicity of the polymer. Accordingly, the stability of dispersions is influenced by the interaction of metal ions with polymers, as it changes the structure of the macromolecule in the solution and the physical and chemical characteristics of the polymer. The study of the interaction of copper nitrate with polymethacrylic acid showed that, depending on the ionic strength of the solution and the pH of the medium, copper (II) complex formation with the polymethacrylic acid with one or two carboxyl groups of polymer is possible [5].In this case, the reaction proceeds in two stages [10]. At high concentrations of copper ions (II), products with a ratio of carboxyl groups of polymer and copper ions (II) equal to 1:1 are formed at low concentrations of copper ions (II) -2:1 [9]. Investigation of the viscosity of polymethacrylic acid solutions in the presence of copper ions (II) and in their absence showed [10] that its molecular weight increases due to the formation of bonds between two macromolecules, and each metal ion interacts with one or two and four carboxyl groups of a polymer [11-12]. The activation energy of the chelating of copper ions (II) with polyacrylic acid is 24-28 kJ/mol. [3].

Investigation of the process of formation of complexes of carboxyl-containing polymers with heavy metal ions at higher temperatures and a higher ratio of functional groups of polymer and metal ions is practically not studied as well as investigation of colloidal and chemical properties of copper(II) salt precipitate formation with polyacids. Therefore, the purpose of this work is to study the process of interaction of copper ions (II) with polyacrylic acid.

2. Experimental

For investigation of the formation of complexes of carboxyl-containing polymers with heavy metal ions, a solution of polyacrylic acid was used, which was obtained by radical polymerization at the initiation of potassium persulfate and re-deposited with hydrochloric acid with a molecular weight of $1.6 \cdot 10^6$, a polymer concentration of 120 g/L and anhydrous copper sulphate (II) grade hc.

The complexation reaction was carried out in two steps: a solution of polyacrylic acid at a concentration of 30 g/L was neutralized with a 10% solution of sodium hydroxide to a predetermined pH. Then, at constant stirring and at 22°C, a specific amount of 10% copper sulfate (II) solution and 10% solution of sodium hydroxide were added dropwise to the solution of polyacrylic acid so that the pH of the mixture was within ± 0.2. The resulting mixture was maintained at stirring for 2 hours and, if necessary, adjusted the pH of the solution. The concentration of polyacrylic acid was varied in the range from 2.2 to 17 g/L, copper sulfate (II) - from 2.3 to 9.6 mmol/L, and sodium hydroxide - from 3 to 380 mmol/L. At high concentrations of sodium hydroxide and pH higher than 11, the conversion was carried out on the concentration of free sodium hydroxide.

The resulting solution was transferred to a pre-heated reactor (50-80)± 0.10°C, from which samples were sampled at certain intervals and cooled to room temperature using ice. The concentration of complexes in the solution was measured spectrophotometrically on the Specord M-80.

At intense coloring of the solution, the sample was diluted with distilled water to the measuring concentration, and the optical density of the initial solution was calculated by the formula:

$D = \mathrm{D}_i\,(V_0 + V_{H_2O}) / \mathrm{V}_0$,

where D_i – measuring the optical density of the dilute solution; V_0–volume of the sample taken from the reactor; V_{H_2O} – volume of water added to the sample.

The viscosity of aqueous solutions of polyacrylic acid and its complexes with copper(II) was measured on a viscometer Bischofa with a capillary diameter of 0.73 mm at a temperature of 22°C.

3. Results discussion

In the interaction of polyacrylic acid at a concentration of 12 g/L with copper ions (II) in a wide range of pH, complexes are formed. With a low degree of ionization of carboxyl groups of polyacrylic acid, the low solubility of complexes with a low concentration of copper(II), and pH <4, the precipitate of complexes is formed (Fig. 1, curve 1). At higher pH values, water-soluble copper complexes (II) with polyacrylic acid are formed. The solubility of such complexes depends on the number of ionized carboxyl groups of the macromolecule. On the ratio of the concentration of carboxyl groups to the concentration of copper ions (II), equal to 3.3 and pH 6.2, the solubility of the complexes is preserved.

From Figure 1 (curve 2), it is seen that the viscosity of aqueous solutions of polyacrylic acid decreases with the increasing concentration of copper ions (II) in the solution. This confirms the formation of transverse bonds between the monomeric portions of polyacrylic acid and the reduction of the size of the macromolecule in the solution. At the concentration of copper ions (II) in the solution above 50 mmol/L, the system viscosity increases as a result of the formation and aggregation of insoluble copper (II) complexes with polyacrylic acid. At pH of the solution above 10 complexes of copper(II) with polyacrylic acid were partially destroyed with the formation of copper hydroxides (II).

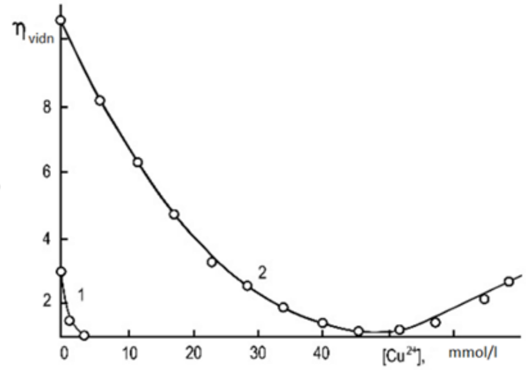

Fig.1. Dependence of the relative viscosity of the complex of polyacrylic acid with copper on the concentration of copper ions (II) in a solution of polyacrylic acid at pH 3.0 (1) and 6.2 (2)

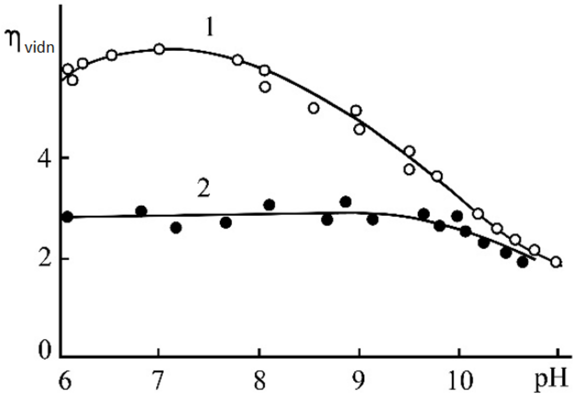

Fig.2. Dependence of the relative viscosity of the solution of polyacrylic acid (1) and its complex with copper (II) (2) on the pH of the mixture

The viscosity of solutions of copper(II) complexes with polyacrylic acid at a concentration of polyacrylic acid 8.5 g/L and copper ion (2.3)/2.3 mmol/L practically does not change with an increase in the pH of the solution from 6 to 10 (Fig. 2, curve 2), while the viscosity of the polyacrylic acid solution is noticeably reduced. This indicates the stability of such complexes in this pH range.

Investigation of complex formation of polyacids with copper ions (II) showed [9,11,13-14] that at low concentrations of copper ions (II) in the mixture complexes associated with two carboxyl groups of polyacids are formed, while at high concentrations ions of copper (II), one copper ion (II) binds to only one carboxyl group, and hydroxy complexes of copper (II) are formed. In the latter case, the formation of hydroxyls between two copper ions (II) is possible. Formation of hydroxides between two ions of copper (II) obviously proceeds by reaction:

$$2[(RCOO)Cu(OH)(H_2O)_3] \boxed{\leftrightarrow} [(RCOO)Cu(H_2O)_2(OH)_2Cu(H_2O)_2(RCOO)] + H_2O$$

In the case of excess copper ions (II) in the solution, there is a reaction of the formation of copper hydroxides (II) and the formation of polyions of type: $[Cu_m(OH)_y(H_2O)_{4m-y}]^{(2m-y)+}$. These polyions are adsorbed on the macromolecules of polyacrylic acid complexes with copper(II), forming highly insoluble hydrated particles.

Also, in Figure 3 (curve 1), it is shown that the interaction of polyacrylic acid with copper sulfate (II) (initial concentration of copper sulfate (II) in solution 62 (mmol L^{-1})) leaves the precipitate of insoluble polyacrylate copper salts. With the increase in the concentration of polyacrylic acid, the concentration of bound copper ions (II) in the mixture decreases and reaches a minimum for the molar ratio of carboxyl groups of polyacrylic acid and bound copper ions equal to 2. This ratio indicates the formation of chelates, in which the copper ion binds two carboxyl groups of the polyacid, which coincides with the literature data [11,15].

With an increase of the pH of the solution, there is an increase in the concentration of bound copper and a decrease of the initial concentration of polyacrylic acid in the solution. There is a linear relationship between the amount of bound copper and the pH of the medium (Fig. 3, curve 2).

Obviously, polyacrylic acid helps to precipitate the main copper salts, which are formed as a result of hydrolysis of copper sulfate (II) in dilute aqueous solutions.

.

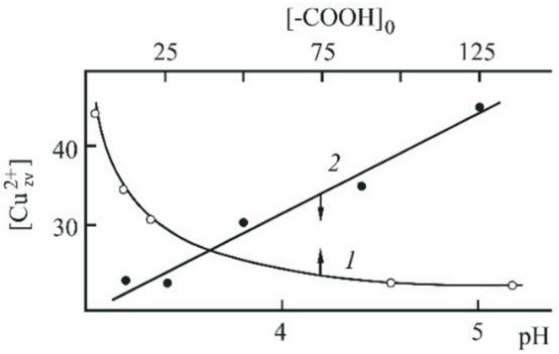

Fig. 3 Dependence of the concentration of bound ions of copper (II) (mmol L^{-1}) from the initial concentration of carboxyl groups of polyacrylic acid in solution (mmol L^{-1}) and pH of the medium

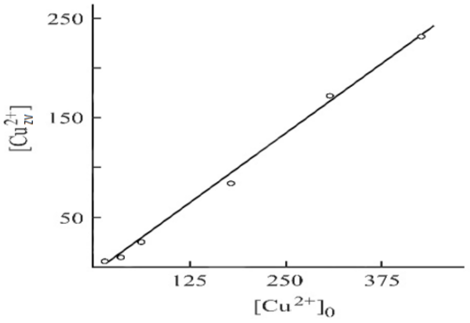

Fig. 4. Dependence of the concentration of bound ions of copper (II) (mmol/L^{-1}) from the initial concentration of copper sulfate (II) in solution (mmol L^{-1})

Indeed, an increase of the initial concentration of copper sulfate (II) in the solution at the constant concentration of polyacrylic acid leads to a linear increase in the concentration of bound ions of copper (II) (Fig. 4).

Figure 5 (curve 1.2) shows that the plateau at a pH close to 5, which is associated with the formation of copper salts with polyacrylic acid (initial concentration of copper hydroxide (II) in the dispersion of 6.3 g L-1). The molar ratio of copper ions to carboxyl groups of polyacrylic acid is equal to 1. This suggests that at pH of the medium within the limits of 4.5-5, the basic copper(II) salts of polyacrylic acid are formed. An increase in the concentration of polyacrylic acid leads to a decrease in the length of the plateau, which is associated with the change in the size of the globule of the macromolecule in the solution.

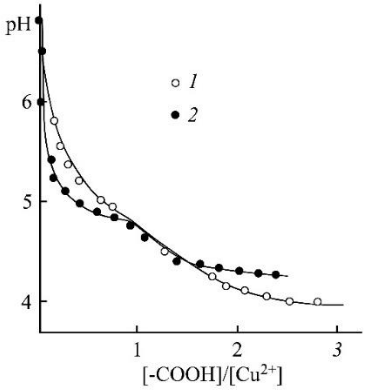

Fig. 5. Titration curves of copper (II) hydroxide dispersion with polyacrylic acid (1,2). Concentrations [-COOH], [Cu^{2+}] (mmol L^{-1})

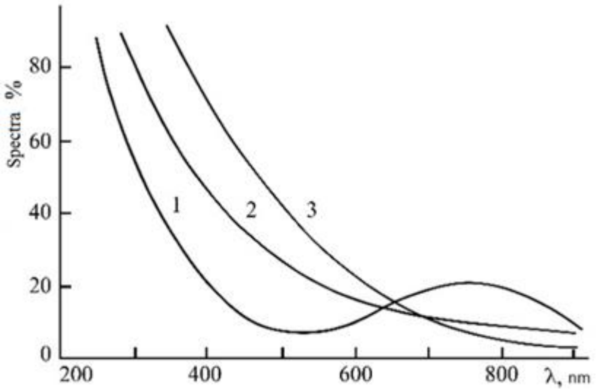

Fig. 6. The spectra of the polyacrylic acid complex with copper at room temperature (1) and after heating at 70°C for 20 (2) and 100 min. (3) pH 9.5

When heating aqueous solutions of complexes of copper (II) with a concentration of copper ion (II) -2.3 mmoles/L and polyacrylic acid (concentration of polyacrylic acid 17 g/L) to $55^{o}C$ at pH> 8, the color of the solution varies from blue to light brown.

The results of spectrophotometric studies showed that the absorption band disappears in the range of 700-800 nm. This is typical for hydrated copper ions (II). The absorption intensity in the region below 600nm increases significantly (Fig. 6) with an increasing degree of transformation of the complex. At low initial concentrations of copper ions (II) in solution, the solubility of the complexes is not reduced, and there is no observed formation of the sediment of copper compounds (II).

The solutions are kept unchanged for several months because when the complexes of copper (II) with polyacrylic acid are heated, the weakly bound water in the inner sphere evaporates:

$$[(RCOO)Cu(OH)(H_2O)_3] \boxed{\leftrightarrow} [(RCOO)Cu(OH)(H_2O)] + H_2O$$

Also possible reactions:

$$[(RCOO)Cu(OH)_2Cu(RCOO)] \boxed{\leftrightarrow} [(RCOO)CuOCu(RCOO)] + H_2O$$

Analyzing literary data, it can be argued that similar reactions are observed when heating copper (II) complexes with acetic acid [9]. Figure 7 shows the dependence of the optical density on the wavelength of 550 nm of the complex of copper ion complex (II) with polyacrylic acid obtained at a concentration of polyacrylic acid 4.3-17 g/L, pH 8.5-10, and heated at 55-80^0 C for 3 hours, from the initial the concentration of a copper ion in the solution (1) and the gradual addition of copper (II) saline solution to the already obtained and heated at 70°C for 2 hours. Copper complex with polyacrylic acid at a concentration of polyacrylic acid 17 g/L, pH 9.6.

Upon completion of the reaction, the absorption rate in the region of 550 nm is almost proportional to the concentration of copper ions (II) in the mixture and is almost independent of the concentration of polyacrylic acid and the pH of the mixture within 8-11. (Fig. 7, line 1).

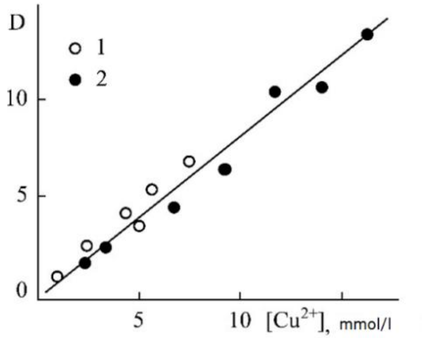

Fig. 7. Dependence of the optical density of the solution of copper ion complex (II) with polyacrylic acid at a wavelength of 550 nm

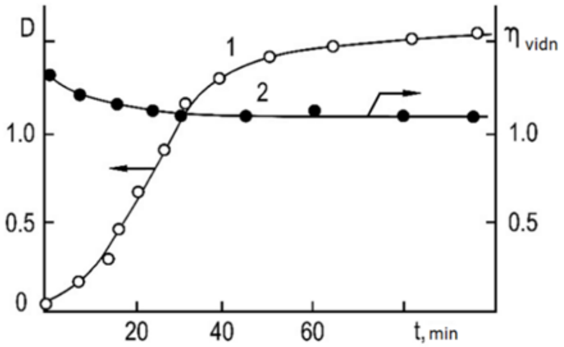

Fig. 8. The change in the optical density of the solution of the complex of polyacrylic acid with copper (1) and its relative viscosity (2) overtime at an initial concentration of polyacrylic acid 2.7 g/L, copper ion (-2) -2.3. mmol/L, pH 9.2, temperature 70^{0}C, and a wavelength of 430 nm

Similar data are obtained in the process of studying the formation of copper complexes with dendrimers of polyamidoamine and polypropylene imine [7,16]. The interaction of copper salts (II) with compounds obtained by heating copper(II) complexes with polyacrylic acid at 70°C leads to an increase of absorption intensity in the region below 500 nm. Dispersions of copper oxides are not formed at concentrations of copper ions (II) 14-15 mmol/L (Fig. 7, line 2). At the concentration of copper ions (II) above 18 mmol/L, after cooling the mixture, a dispersion with copper oxide particles (II) is formed and stabilized with copper (II) complex with polyacrylic acid. The addition to the dispersion of the ammonia solution leads to its rapid dissolution and the formation of a solution of light blue.

Investigation of the process of dehydration of complexes showed that on the curves in Figures 8 and 9, it is possible to conditionally distinguish three areas: the rapid growth of the speed associated with heating the reaction mixture to a given temperature, the area of constant velocity and the deceleration area associated with the flow of hydrated complex of copper(II) with polyacrylic acid.

It should be noted that during the reaction, the viscosity of the solution slightly decreases (Fig. 8, curve 2). During the reaction, the viscosity of the solution slightly decreases (Fig. 8, curve 2). An increase in the temperature of the mixture, the initial concentrations of copper ions (II) and polyacrylic acid, and pH lead to an increase in the reaction rate on the linear region of the curve (Fig. 9). Initial concentrations of polyacrylic acid 17g/L, copper ion (II) 6.9 mmol/L, pH of the mixture is 10, the temperature of the reaction mixture is 80 (1) 72 (2), 65 (3), 55 (4)°C, and the wavelength is 430 nm. The calculated effective energy of the process activation is equal to 39 ±6 kJ/mol.

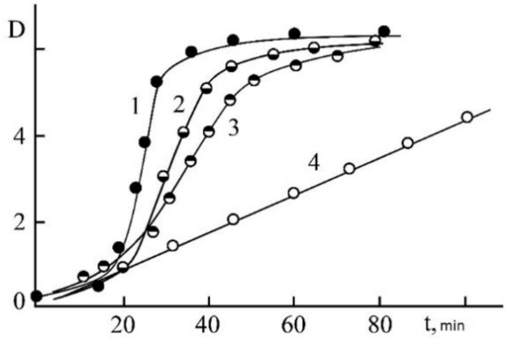

Fig.9. Change in time of optical density of a solution of the polyacrylic acid complex with copper at a temperature of 80 (1) 72 (2), 65 (3), 55 (4)^{0}C

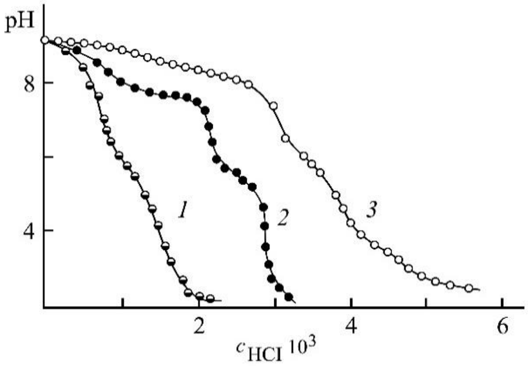

Fig.10. Titration curves of dispersion of copper hydroxide (II) with polyacrylic acid

The reaction of copper ammonium complexes with ammonium salts of polyacrylic acid at a lower pH of the solution was investigated. The results of the titration of ammonium polyacrylate with hydrochloric acid (Fig. 10, curve 1) show that at a pH close to 6, the bend is observed on the curve, which is associated with conformational changes of the macromolecule of polyacrylic acid. At pH 2.5-3, a precipitate of polyacrylic acid is formed. On the curve titration of the ammonia complex with copper hydrochloric acid, there are two plateaus (Fig. 10, curve 2). The first plateau is observed at a pH close to 8, which is associated with the formation of salts of the ammonia complex of copper and hydrochloric acid. The second plateau is observed at pH 5-5.5 and complete destruction of the complex and formation of copper hydroxide sediment. Further decrease of the pH value leads to the dissolution of the sediment and the formation of copper chloride.

Titration with a solution of hydrochloric acid of a mixture of ammonia polyacrylate and the ammonia complex of copper showed (Fig. 10, curve 3) that in the first stage at pH close to 8, the salts of the ammonia complex of copper with polyacrylic acid are formed. Further reduction of the pH of the solution leads to the gradual disintegration of the ammonia complex of copper and the formation of basic copper salts with polyacrylic acid. The precipitation of copper polyacrylates is observed only at a pH of 3-3.5. The light green color of the solution above the precipitate at pH 3 indicates the partial formation of copper chloride.

4. Conclusions

The complex formation of copper ions with polyacrylic acid has been studied. It is shown that complex compounds are formed when copper ions (II) interact with polyacrylic acid in a wide range of pH. At pH <4, a precipitate of complex compounds is formed, whereas when the pH is increased, water-soluble copper(II) complexes with polyacrylic acid are formed. The solubility of such complexes depends on the number of ionized carboxyl groups of the macromolecule.

Investigation of the complex formation of polyacids with copper ions (II) showed that at low concentrations of copper ions (II) in the mixture, complexes associated with two carboxyl groups of polyacids are formed in the mixture, while at high concentrations of copper ions, one ion of copper(II) binds to only one carboxyl group and hydroxy complexes of copper(II) are formed. When heating aqueous solutions of copper(II) complexes with polyacrylic acid, weakly bound water in the internal sphere is lost.

Formation of copper oxide dispersion is not observed at higher concentrations of copper ions (II) in the interaction of copper(II) complexes with polyacrylic acid.

After cooling the mixture, a dispersion with copper oxide particles (II) is formed and stabilized with copper (II) complex with polyacrylic acid. Addition to the dispersion of the ammonia solution leads to its rapid dissolution and the formation of a solution of light blue.

References

[1] Esumi K, Ogihara K, Meguro K. Pigment Wetting and Dispersing Additives for Water-Based Coatings and inks. International Journal of Molecular Sciences, 2013; 14(12): 23597-23613.

[2] Starchevskyy V, Bernatska N, Typilo I, Oliynyk L, Kvit R. Determination of the Cavitation Influence on the Destruction Process of Microorganism Cells Agglomerates. Chemistry and Chemical Technology, 2018; 12: 462-465.

[3] Aneli J, Shamanauri L, Markarashvili E, Tatrishvili T. Polymer-silicate composites with modified minerals. I. Chemistry and Chemical Technology, 2017; 11: 201-209.

[4] Dzhardymalyeva H, Pomohailo A. Monomeric and polymeric metal carboxylates. Fyzmatlyt, Moscow, 2009: 400 p.

[5] Mandel M, Leyete JC. Interaction of poly(methacrylic acid) and bivalent counterions.: Journal of Polymer Science Part A., 1964; 2: 2883-2887.

[6] Skopenko VV, Tsyvadze AIu, Savronskyi LY, Harnovskyi AD. Coordination chemistry. Moscow, 2007: 427 p.

[7] Crooks RC, Zhao M, Sun L, Chechik V, Yeung LK. Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Applications to Catalysis. Accounts of Chemical Research, 2001; 34: 181-190.

[8] Pomohailo AD, Rosenberg S, Uflyand IE. Metal nanoparticles in polymers. Moscow, 2000: 672 p.

[9] Kislenko VN, Oliynyk LP. Complex Formation of Polyethyleneimine with Copper(II), Nickel(II), and Cobalt(II) Ions. Journal of Polymer Science Part A: Polymer Chemistry, 2002; 40: 914-922.

[10] Kolawole EG, Bello MA. Interaction of Divalent Ions of Copper, Magnesium and Zinc with Isotactic Polymethacrylic Acid. European Polymer Journal, 980; 16: 325-332.

[11] Lázaro-Martínez JM, Monti GA, Chattah AK. Insights into the coordination sphere of copper ion in polymers containing carboxylic acid and azole groups. Polymer, 2013; 54 (19): 5214-5221.

[12] Annenkov VV, Danilovtseva EN, Saraev VV, Mikhaleva AI. Complexation of copper(II) ions with imidazole–carboxylic polymeric systems. Journal of Polymer Science Part A: Polymer Chemistry, 2003; 41: 2256-2263.

[13] Kolawole EG, Mathieson SM. Binding of Cu(II) to poly(methacrylic acid). Journal of Polymer Science Part A: Polymer Chemistry, 1979;17(9): 557-573.

[14] Filenko M, Demchenko Z, Mustafaeva M. Behavior of ternary complexes: bovine serum albumin – Cu^{2+}-copolymers of acrylic acid with N-isopropylacrylamide (fluorescent approach). Biomacromolecules, 2001; 2(1): 72-81.

[15] Bekturov EA, Bymendyna LA, Mamytbekov HK. Complexes of water-soluble polymers and hydrogels. Almata, 2002, 202 p.

[16] Bymendyna LA, Yashkarova MH, Kudayberhenov SIe, Bekturov EA. Polymer complexes (preparation, properties, application). Semypalatynsk, 2003, 285 p.

To whom correspondence should be addressed: Dr. Lilianna Oliynyk, Lviv National Polytechnic University, 12, Bandera str., 79013 Lviv, Ukraine, E-mail: *lilianna.p.oliynyk@lpnu.ua*