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SYNTHESIS AND CHARACTERIZATION OF COPPER(II) CHLORIDE COMPLEXES WITH NON-IONIC POLYMERS PEG AND PVP

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Abstract. The compositions of polymer-metal complexes based on copper (II) chloride and polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) have been determined by the potentiometric method. Based on the experimental data, obtained to determine the composition of the complex, the titration curves have been plotted, and the optimal molar ratios of the reacting components have been found. The Bjerrum's formation functions have been calculated. The obtained data indicate the formation of the polymer copper complexes, in which there are two PEG mono-links per two copper ions-complexing agent (1:2 in the Cu^{2+}-PEG), and in the case of PVP, there are three ones (1:3 in the Cu^{2+}-PVP). On the basis of thermodynamic constants of stability, using isotherm equations and isobars of Vant Hoff and Gibbs, Gibbs' energy (Δ_rG^0), enthalpy (Δ_rH^0) and entropy (Δ_rS^0) changes have been calculated. The complexation process in the Cu^{2+}-PEG and Cu^{2+-}PEG systems is characterized by negative Gibbs' energies, which indicates a spontaneous occurrence of the polymer-metal complex (PMC) formation process in these systems. In contrast, the complexation of copper ions with PEG is accompanied by the large positive enthalpy values, which indicate that the interaction of Cu^{2+} with the functional groups of the polymer is energetically unfavorable. The entropy values are positive, which can be explained by the dehydration of ions and functional groups, acting as ligands and a chelating effect during complexation, when one ion binds to several functional groups. The structure of the synthesized complexes has been investigated by IR spectroscopy.

Keywords: polyvinylpyrrolidone, polyethylene glycol, copper, complexation, stability constants, composition.

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1. Introduction

The study of the interactions of metal ions with polymers in solutions is an actual task, the solution of which will allow one not only to deepen the knowledge of the reactions in the solutions, but also to find new solutions to some technical problems, such as, for example, increasing the efficiency of water purification from metal ions, creating new sensors or biomedical diagnostic labels and active catalysts. The properties of such systems are largely determined by the interaction between the ions and polymer in the aqueous solutions, which includes the hydration of ions and polymer macromolecules, complexation, and electrostatic interaction [1].

The main characteristic of the interaction of metal ions-complexing agent with the polymer ligands is the constant of complexation, which, according to the main provisions of physical chemistry [2], is associated with the standard change in the Gibbs' energy during the reaction. This value is integral and depends on the change in both the enthalpy and entropy during binding. The enthalpy and entropy contributions to the Gibbs' energy of complexation are usually not specially estimated. Even for low molecular weight complexes, such data are rare in the literature [3].

Meanwhile, for the polymer-salt systems, the values of enthalpy and entropy of complexation are of particular interest, since they make it possible to clarify the complex mechanism of the interaction of ions with macromolecules. The copper (II) complexes are characterized by high activity and selectivity in various processes due to the metal-ligand interaction [4-6]. The ligands PEG and PVP are also widely used as ligands [7-9]. In turn, the mixtures of copper with PEG and PVP are widely used today as catalysts for the C–N bond formation, cross-coupling reactions, azide-alkyne cycloaddition, synthesis of substituted imidazoles and indole [10-14]. Earlier, the polymer-metal complexes based on palladium (II), iron (III) chloride and polyvinylpyrrolidone were synthesized and their structure was studied [15,16]. A palladium-polyvinylpyrrolidone complex $PdCl_2$-PVP demonstrated catalytic activity in the oxidation of octene-1 [17]. There are practically no data on the thermodynamic data on the complexation of PEG and PVP with the copper (II) ions in the aqueous solutions.

The aim of this work is to present the results of studying the complexation process, using the potentiometric method, comparing the thermodynamic characteristics (Gibbs'energy, enthalpy, entropy) of the complexation process of the copper (II) ions with the water-soluble non-ionic polymers PEG and PVP, and the investigation of the morphology of the copper polymeric complexes. A comparative analysis of the thermodynamic parameters of the formation of the polymer complexes of copper (II) has been carried out and their stability has been assessed.

2. Experimental part

Copper chloride $CuCl_2{\cdot}2H_2O$, polyethylene glycol (molecular weight 10,000, Aldrich), polyvinylpyrrolidone (molecular weight 40,000, AppliChem, Germany), hydrochloric acid, nitric acid, sodium chloride, sodium nitrate were used without a preliminary purification.

The processes of complexation of the copper (II) ions with PEG and PVP were studied by the potentiometric method [18]. Potentiometric studies were carried out under the thermostated conditions on a pX-150MI ion meter, using silver chloride and glass electrodes. The pH measurement accuracy was 0.02 pH units. The IR spectra of the PEG, PVP ligands and Cu (II)–PEG and Cu (II)–PVP complexes were recorded on a JASCO FT IR-4100 type A instrument in the range 4000-450 cm^{-1}. The stability constants of the PMC were calculated on the basis of the modified Bjerrum's method [19, 20]. The SEM images were obtained with a JSM-6490LA Jeol instrument. The IR spectra and SEM images were obtained in the analytical laboratories at the Technical University of Kaiserslautern (Germany).

The complexes $CuCl_2$-PEG and $CuCl_2$-PVP were prepared by mixing the aqueous solutions of $CuCl_2 \cdot 2H_2O$ and PEG and PVP at the optimal molar ratios of 1:2 and 1:3, respectively. The resulting mixtures were stirred on a magnetic stirrer for 1 hour at the room temperature. The resulting complexes were dried and stored in air at the room temperature. The yield was 97%.

3. Results and discussion

Figures 1 and 2 show curves of potentiometric titration of PEG with nitric acid (Fig. 1), and PVP with hydrochloric acid in the absence and in the presence of Cu^{2+} ions at T = 298 K, I = 0.10 mol/L (potentiometric titration curves for other values of temperature and ionic strength have a similar form).

As can be seen from Figures 1 and 2, the titration curves in the presence of metal ions, the complexing agent, are in a more acidic region than in their absence. This fact indicates the presence of a complexation process between the polymer ligand and the metal ion.

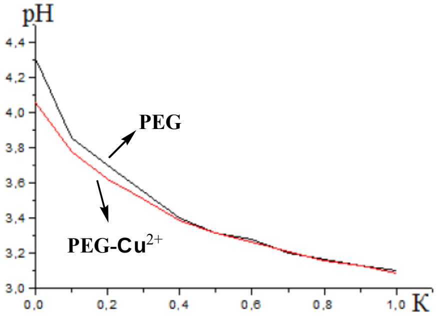

Figure 1 – The curve of pH-potentiometric titration of the PEG-Cu^{2+} complex with nitric acid ($C(HNO_3) = 1 \cdot 10^{-2}$ mol/L)

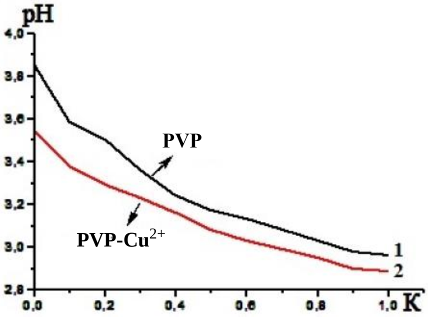

Figure 2 – The curve of pH-potentiometric titration of the PVP-Cu^{2+} complex with hydrochloric acid ($C(HCl) = 1 \cdot 10^{-2}$ mol/L)

To interpret the displacement of the titration curves, a modified Bjerrum's method has been used, the data of which are presented in Table 1. The calculated data confirm the formation of a polymer-metal complex (PMC) in a ratio of 1:2 in the Cu^{2+}-PEG system, 1:3 in the Cu^{2+}-PVP system [21, 22]. It is known that the transition metal ions, interacting with polymers may not realize their maximum coordination number, since the copper ions can be saturated with the coordination due to anions or solvent molecules [19].

Also, the steric repulsion between large ligands and electrostatic mutual repulsion of ligands – anions, when they are replaced by the water molecules at a positively charged metal ion, can prevent the coordination of additional ligands [23].

Table 1 – Calculated values of the Bjerrum's formation functions of the PEG -$CuCl_2$, PVP-$CuCl_2$ system (T = 298 K, I = 0.10 mol/L)

System	$[LH^+]$ [a] mol/L	$[L]$ [b] mol/L	$[L_c]$ [c] mol/L	pL [d]	n [e]
PEG– Cu^{2+}	$2.26 \cdot 10^4$	$13.49 \cdot 10^4$	$1.76 \cdot 10^3$	2.87	1.13
	$5.37 \cdot 10^4$	$16.22 \cdot 10^4$	$1.17 \cdot 10^3$	2.79	0.75
	$8.37 \cdot 10^4$	$10.72 \cdot 10^4$	$1.42 \cdot 10^3$	2.97	0.91
	$11.46 \cdot 10^4$	$8.91 \cdot 10^4$	$1.29 \cdot 10^3$	3.05	0.83
	$14.56 \cdot 10^4$	$7.24 \cdot 10^4$	$1.15 \cdot 10^3$	3.14	0.74
	$17.64 \cdot 10^4$	$5.89 \cdot 10^4$	$0.98 \cdot 10^3$	3.23	0.63
	$20.74 \cdot 10^4$	$4.90 \cdot 10^4$	$0.77 \cdot 10^3$	3.31	0.49
	$23.95 \cdot 10^4$	$4.79 \cdot 10^4$	$0.46 \cdot 10^3$	3.32	0.29
PVP –Cu^{2+}	$0.99 \cdot 10^{-4}$	$3.46 \cdot 10^{-1}$	$9.00 \cdot 10^{-4}$	0.46	2.70
	$1.99 \cdot 10^{-4}$	$2.81 \cdot 10^{-1}$	$8.01 \cdot 10^{-4}$	0.55	2.40
	$2.99 \cdot 10^{-4}$	$0.76 \cdot 10^{-1}$	$7.02 \cdot 10^{-4}$	1.12	2.10
	$3.97 \cdot 10^{-4}$	$0.69 \cdot 10^{-1}$	$6.03 \cdot 10^{-4}$	1.16	1.80
	$4.97 \cdot 10^{-4}$	$0.71 \cdot 10^{-1}$	$5.03 \cdot 10^{-4}$	1.15	1.50
	$5.96 \cdot 10^{-4}$	$0.68 \cdot 10^{-1}$	$4.03 \cdot 10^{-4}$	1.17	1.20

Note. [a] $[LH^+]$ – the concentration of the protonated ligand groups; [b] [L] – the concentration of the free ligands which are not involved in a complexing process; [c] $[L_C]$ – the concentration of the ligand groups connected in a complex; [d] pL – the concentration of the free ligands calculated on Henserson-Hasselbach equation pH = pKα + mlg[L]/[LH+], where m - the empirical coefficient considering interlink interaction of a polymeric chain; [e] n – Bjerrum's formation functions or average coordination number of a metal ion.

The thermodynamic parameters of the complexation of high-molecular ligands with the copper ions were also calculated, using the classical laws of thermodynamics for the systems with polymer ligands.

The results of our studies have shown that the complexation process in the Cu^{2+}-PEG and Cu^{2+-}PVP systems is characterized by negative Gibbs' energies, which indicates a spontaneous occurrence of the PMC formation process in these systems (Table 2).

The process of binding ions by the functional groups of the polymer leads to a limitation of ion mobility, is entropically unfavorable, and contributes to a decrease in entropy. However, in the systems under study, the entropy values are positive. This phenomenon can be explained by a number of reasons: first, this is due to the dehydration of ions and functional groups acting as ligands. In this case, the released water molecules acquire translational mobility, resulting in an increase in entropy [24]; secondly, it is a chelating effect during complexation, when one ion binds to several functional groups.

For low molecular weight systems, it has been shown that the formation of chelate complexes is accompanied by an increase in entropy. As an explanation of this effect, it is indicated in the literature that the occupation of several coordination centers of the complexing ion by the functional groups, belonging to one ligand molecule is entropy advantageous, since dehydration releases more water molecules than when the ligand molecules are bound [1].

The reaction of complexation of the copper ions with PVP is accompanied by an exo effect, as evidenced by the negative value of the enthalpy. As the temperature rises, the stability of this complex decreases.

In contrast to the system, based on Cu^{2+}-PVP, the complexation of the copper ions with PEG is accompanied by large positive enthalpy values, which indicate that the interaction of Cu^{2+} with the functional groups of the polymer is energetically unfavorable. The positive value of the enthalpy for this system indicates cooperative structural changes in the solution, accompanied by a gain in entropy.

Table 2 – Thermodynamic characteristics of the complexation process of the Cu^{2+} ions with PEG and PVP.

Complex	T, K	$\lg\beta^{0\,a}$	$-\Delta_rG^{0\,b}$, kJ/mol	$\pm\Delta_rH^{0\,c}$ kJ/mol	$\pm\Delta_rS^{0\,d}$ J/mol·K
PEG-Cu^{2+}	298	5.98±0.06	34.11±0.42	117.3±0.11	501.05±0.15
	318	6.10±0.07	35.98±0.41		
	343	7.25±0.09	44.13±0.45		
PVP–Cu^{2+}	298	14.50±0.19	82.72±0.09	175.7±0.30	218.62±0.94
	308	14.40±0.18	84.91±0.11	487.5±0.80	1307.13±0.57
	318	11.50±0.25	71.83±0.08	244.9±0.90	544.26±0.30

Note. $^a\beta^0$ is the thermodynamic stability constant of the complexes. $^b\Delta_rG^0$ is the change in the Gibbs' energy of the reaction. $^c\ \Delta_rH^0$ is change in the enthalpy of reaction (thermal effect). $^d\ \Delta_rS^0$ is the change in the entropy of the reaction.

IR spectroscopy is one of the simplest methods for determining the functional groups of a polymer ligand, which are involved in the formation of a coordination bond with a complexing metal. The IR spectra of PEG and Cu^{2+}-

PEG are shown in Figures 3 and 4. The bands due to the C–O stretching mode were merged in the very broad envelope, centered on 1242 and 1089 cm^{-1} arising from C–O, C–O–C stretches, and C–O–H bends vibrations of $CuCl_2$ in PEG [22, 25, 26].

The IR spectra have shown the existence of the van der Waals interactions between the chain of PEG and $CuCl_2$.The shift of peaks corresponding to the vibrations of the carbonyl group of the polymer to the lower frequency region is due to the formation of the coordination bond due to the donor – accepter interaction between the O atom of the PEG polymer ligand and ions Cu(II).

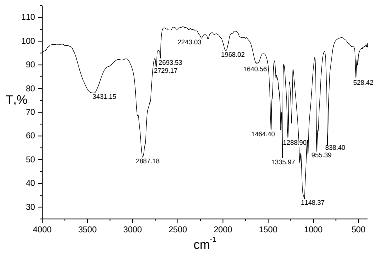

Figure 3 – The IR – spectrum polyethylene glycol

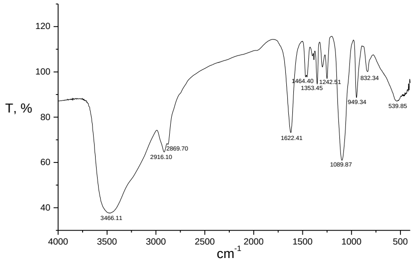

Figure 4 – The IR – spectrum of the complex $CuCl_2$-PEG

As seen from the IR spectra (Figures 5 and 6), the peak characteristic of the C=O bond in PVP becomes asymmetric after the addition of metal chlorides, which indicates a strong interaction between PVP and Cu (II) ion in the PVP-$CuCl_2$ complex. The IR spectra of the studied complex based on copper (II) chloride and PVP contain a band at 3400 cm^{-1}, which is characteristic of PVP. The carbonyl group in PVP is characterized by a peak at 1651 cm^{-1}, broadened due to the C=N bond in the lactam ring. This band shifts to 1510–1645 cm^{-1} in the complex [21, 22, 27, 28].

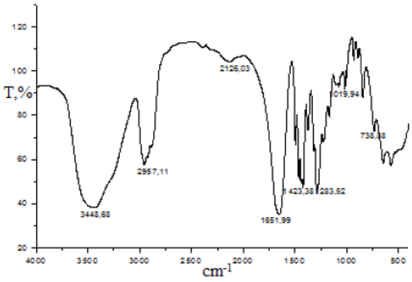

Figure 5 – The IR-spectrum polyvinylpyrrolidone

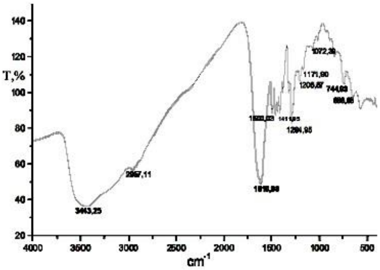

Figure 6 – The IR-spectrum of the complex $CuCl_2$-PVP

The differences in the IR spectra of PEG and the PEG-$CuCl_2$ complex, as well as PVP and PVP-$CuCl_2$ coordination compound, are observed as a result of the donor-acceptor interaction between the O atom in the PEG and PVP polymer ligands and the metal ion.

Based on the results of the studies carried out, taking into account the literature information [29, 30] and that chlorine anions do not form a complex with polymers, the following schemes of the interaction between the components of the Cu^{2+}-PEG and Cu^{2+}-PVP systems can be presented (Figure 7):

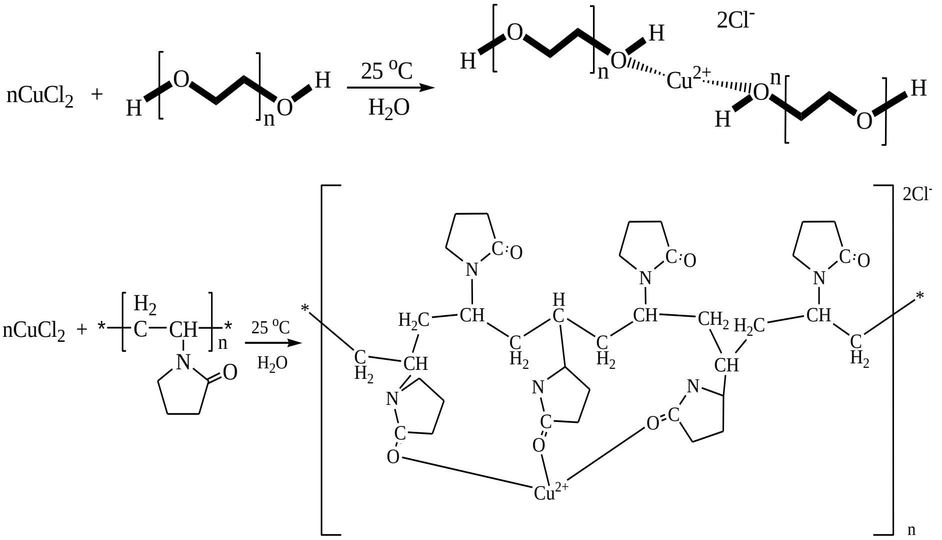

Figure 7 – The interaction between the components of the Cu^{2+}-PEG and Cu^{2+}-PVP systems

The proposed mechanism of interaction of the copper ions with PEG and PVP is similar and the following stages were suggested: the formation of Cu-Cl-PEG/or PVP bridge, and the formation of Cu-ion which is coordinated by two oxygen atoms of PEG or three oxygen atoms of PVP and two chlorine ions [22].

To study the surface of the polymer-metal complexes of copper (II), the method of scanning electron microscopy has been used (Figures 8, 9). An analysis of the micrographs indicates the formation of the polymer films with a porous inhomogeneous amorphous structure.

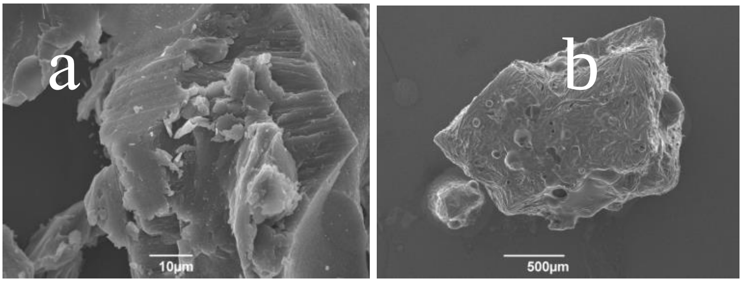

Figure 8 – Micrographs of the PEG and PEG-$CuCl_2$ complex

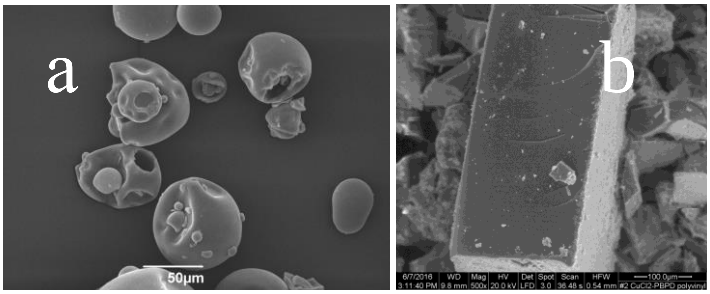

Figure 9 – Micrographs of the PVP and PVP-$CuCl_2$ complex

4. Conclusion

The present study describes the synthesis and characterization of the copper (II) complexes with the non-ionic water-soluble polymers PEG and PVP. From the IR spectra it may be concluded that the polymer ligands act as a chelating agent to the metal ion and bind through the oxygen atoms of the C=O group. Scanning electron microscopy confirms the coordination of the polymer ligands PEG and PVP, and the amorphous structure of the polymer copper complexes. The calculated data indicate the formation of the coordination compounds in the Cu^{2+}-PEG and Cu^{2+}-PVP systems. The thermodynamic parameters of the complexation processes between ions have been calculated. The stability constant and Gibbs' free energy calculations show that the Cu^{2+}-PVP complex is more stable than the Cu^{2+}-PEG complex. The both complexes are effective co-catalysts for the octene-1 oxidation. The percentage product of reactions shows that the PVP-$CuCl_2$ complex is more active than the PEG-$CuCl_2$ complex.

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Conflict of Interest: The authors declare that there is no conflict of interest between the authors requiring disclosure in this article**.**

МЫС (ІІ) ХЛОРИДІНІҢ ИОНДЫ ЕМЕС ПЭГ ЖӘНЕ ПВП КЕШЕНДІ ҚОСЫЛЫСТАРЫНЫҢ СИНТЕЗІ ЖӘНЕ СИПАТТАМАЛАРЫ

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Түйіндеме. Мыс(ІІ) хлориді және полиэтиленгликоль (ПЭГ) мен поливинилпирролидон (ПВП) негізіндегі кешенді қосылыстардың құрамы потенциометрлік әдіспен анықталған. Кешенді қосылыстың құрамын анықтауға арналған тәжірибелік мәліметтер нәтижесінде титрлеу қисықтары тұрғызылған және әрекеттесуші құраушылардың оптимальді мольдік қатынастары табылған. Бьеррумның түзілу функциясы есептелген. Есептелген мәндер ПЭГ екі монобуыны (Cu^{2+}-ПЭГ кешенді қосылысында 1:2), ПВП үш монобуыны кешентүзгіш мыс иона(Cu^{2+}-ПВП кешенді қосылысында 1:3) сәйкес келетіндігін дәлелдеген. Тұрақтылық константасы негізінде Вант – Гофф және Гиббс изотерма және изобара теңдеулерін қолдана отырып Гиббс энергиясы (Δ_rG^0), энтальпия (Δ_rH^0) және энтропия (Δ_rS^0) мәндері есептелген. Cu^{2+}-ПЭГ және Cu^{2+}-ПВП жүйелеріндегі кешентүзілу үдерісі Гиббс энергиясының теріс мәнімен сипатталады, яғни аталмыш жүйелерде полимерметалдық кешенді қосылыс түзілу үдерісі өздігінен тура бағытта жүреді. Мыс иондарының ПВП кешентүзілу реакциясы экзо – эффектпен өтеді, яғни энтальпия мәні – теріс. Cu^{2+}-ПВП жүйесімен салыстырғанда мыс иондарының ПЭГ кешентүзілу үдерісі энтальпияның жоғары оң мәнімен сипатталады, яғни Cu^{2+} полимердің функциональдық топтармен әрекеттесуі энергетикалық тұрғыдан тиімсіз. Энтропия мәні – оң, аталмыш құбылысты лиганд ретіндегі иондар және функциональды топтардың деградациясымен, бір ион бірнеше функциональды топшалармен байланысатын кешентүзілу барысындағы хелаттық эффектпен түсіндіруге болады. ИҚ – спектроскопия әдісімен синтезделген кешенді қосылыстардың құрылысы зерттелген. Полимерлі лигандтардағы оттегі атомы металл – кешентүзгіш ионымен координациялық байланыс орнатуға қатысатындығы анықталған. Сканирлеуші электрондық микроскоп нәтижесі кеуекті біртекті емес аморфтық құрылымға ие полимерлі қабықшалардың түзілетіндігін көрсетеді.

Түйінді сөздер: поливинилпирролидон, полиэтиленгликоль, мыс, кешентүзілу,тұрақтылық константасы, құрам.

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СИНТЕЗ И ХАРАКТЕРИСТИКА КОСПЛЕКСОВ ХЛОРИДА МЕДИ (II) С НЕИОННЫМИ ПОЛИМЕРАМИ ПЭГ И ПВП

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Абстракт. Составы полимерметаллических комплексов на основе хлорида меди (II) и (полиэтиленгликоля (ПЭГ) и поливинилпирролидона (ПВП)) были установлены потенциометрическим методом. По полученным экспериментальным данным, по определению состава комплекса были построены кривые титрования и найдены оптимальные мольные соотношения реагирующих компонентов. Были рассчитаны функции образования Бьеррума. Рассчитанные данные свидетельствуют об образовании полимерных комплексов меди, в которых на два составных монозвена ПЭГ приходятся два (1:2 в комплексе Cu^{2+}-ПЭГ), а в случае ПВП приходится три иона меди-комплексообразователя (1:3 в комплексе Cu^{2+}-ПВП). На основании термодинамических констант устойчивости, используя уравнения изотермы и изобары Вант-Гоффа и Гиббса, были рассчитаны изменения энергии Гиббса (Δ_rG^0), энтальпии (Δ_rH^0) и энтропии (Δ_rS^0). Процесс комплексообразования в системах Cu^{2+}-ПЭГ и Cu^{2+}-ПВП характеризуется отрицательными значениями энергии Гиббса, что свидетельствует о самопроизвольном протекании процесса образования полимерметаллических комплексов (ПМК) в этих системах. Реакция комплексообразования ионов меди с ПВП сопровождается экзо-эффектом, о чем свидетельствует отрицательное значение энтальпии. В отличии от системы на основе Cu^{2+}-ПВП комплексообразование ионов меди с ПЭГ сопровождается большими положительными значениями энтальпии, которые свидетельствуют о том, что взаимодействие Cu^{2+} с функциональными группами полимера энергетически не выгодны. Значения энтропии положительны, данное явление объясняется дегидратацией ионов и функциональных групп, выступающих в качестве лигандов, и хелатным эффектом при комплексообразовании, когда один ион связывается с несколькими функциональными группами. Методом ИК-спектроскопии было исследовано строение синтезированных комплексов. Установлено, что атомы кислорода полимерных лигандов принимают участие в образовании координационной связи с ионом металла-комплексообразователя. Результаты сканирующей электронной микроскопии свидетельствуют о формировании полимерных плёнок с пористой неоднородной аморфной структурой.

Ключевые слова: поливинилпирролидон, полиэтиленгликоль, медь, комплексообразование, константы устойчивости, состав.

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