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SYNTHESIS AND STUDY OF THE COMPOSITION OF A POLYMERMETALLIC COMPLEX BASED ON COPPER(II) CHLORIDE AND POLYETHYLENE GLYCOL

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Abstract: *Based on copper(II) chloride and polyethylene glycol a polymer-metal complex was synthesized, and its composition was established by potentiometric and conductometric methods. The values of the Bierrum's formation functions were calculated. Titration curves were constructed. The optimal molar ratios of the reacting components were found. The data obtained indicate the formation of polymer complexes of copper, in which two complex mono units of polyethylene glycol account for one metal complexing ion. The coordination saturation of the metal-complexing agent in this complex is due to solvent molecules or the anion of metal salts. The thermodynamic characteristics of the complexation process were calculated:* $\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$. *Negative values of the Gibbs' energy change indicate the potential possibility for the process under study in the direction of the formation of the polymer-metal complex. A positive value of the change in enthalpy (*$\Delta_r H^0$*) in the temperature range 298-318K indicates the endothermic nature of the formation of the polycomplex in the indicated range. Changes in entropy values are associated with the destruction of the solvate shells of the PEG's ligand groups and copper ions, the displacement of solvent molecules and the formation of chelate structures. Using IR spectroscopy, it was confirmed that the oxygen atoms of the polymer ligand are involved in the formation of coordination bonds with the metal complexing ion.*

Key words: *polymer-metal complex, copper(II) ions, polyethylene glycol, thermodynamic characteristics, stability*

МЫС(II) ХЛОРИДІ ЖӘНЕ ПОЛИЭТИЛЕНГЛИКОЛЬ НЕГІЗІНДЕГІ ПОЛИМЕРМЕТАЛДЫҚ КЕШЕНДІ ҚОСЫЛЫСТЫ СИНТЕЗДЕУ ЖӘНЕ ҚҰРАМЫН ЗЕРТТЕУ

Аңдатпа: *Мыс(II) хлориді және полиэтиленгликоль негізіндегі полимерметалдық кешенді қосылыс синтезделген және оның құрамы потенциометрлік және кондуктометрлік әдістермен анықталған. Бьеррумнің түзілу функциясы шамасы есептелген. Титрлеу қисықтары тұрғызылған және әрекеттесуші құраушылардың оңтайлы мольдік қатынастары табылған. Алынған нәтижелер полиэтиленгликольдің екі құрамдық монобуынына кешентүзгіш – металл ионының біреуі сәйкес келетін мыс кешенді қосылысының түзілгендігін дәлелдейді. Кешентүзуші металл ионының координациялық қанығуы аталмыш кешенді қосылыста еріткіш молекуласы немесе металл тұзы анионы негізінде жүзеге асады. Кешентүзілу үдерісінің термодинамикалық сипаттамалары есептелген:* $\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$. *Гиббс энергиясы өзгерісінің теріс мәні зерттеліп отырған үдерістің полимерметалдық кешенді қосылыс түзілу бағытында өту әлеуетін көрсетеді. 298-318 К температура аралығындағы энтальпия өзгерісі (*$\Delta_r H^0$*) оң мәні поликешенді қосылыстың осы аралықтағы түзілуі эндотермиялық сипатта екендігін дәлелдейді. Энтропия мәні өзгерісі ПЭГ лиганд тобы және мыс ионы сольваттық қабатының бұзылуымен, еріткіш молекулаларының ығысуымен және хелатты құрылым түзілуімен сипатталады.*

ИҚ – спектроскопия әдісімен полимер лигандтағы оттегі атомы кешентүзгіш – металл ионымен координациялық байланыс түзетіндігі дәлелденді.

Түйінді сөздер: *полимерметалдық кешенді қосылыс, мыс (II) иондары, полиэтиленгликоль, термодинамикалық сипаттамалар, тұрақтылық*

СИНТЕЗ И ИЗУЧЕНИЕ СОСТАВА ПОЛИМЕРМЕТАЛЛИЧЕСКОГО КОМПЛЕКСА НА ОСНОВЕ ХЛОРИДА МЕДИ(II) И ПОЛИЭТИЛЕНГЛИКОЛЯ

Аннотация: *Синтезирован полимерметаллический комплекс на основе хлорида меди (II) и полиэтиленгликоля, и установлен его состав потенциометрическим и кондуктометрическим методами. Были рассчитаны величины функций образования Бьеррума. Были построены кривые титрования и найдены оптимальные мольные соотношения реагирующих компонентов. Полученные данные свидетельствуют об образовании полимерных комплексов меди, в которых на два составных монозвена полиэтиленгликоля приходится один ион металла-комплексообразователя. Координационная насыщенность металла-комплексообразователя в этом комплексе осуществляется за счет молекул растворителя или аниона солей металла. Рассчитаны термодинамические характеристики процесса комплексообразования:* $\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$. *Отрицательные значения изменения энергии Гиббса указывают на потенциальную возможность протекания исследуемого процесса в направлении образования полимерметаллического комплекса. Положительное значение изменения энтальпии* ($\Delta_r H^0$) *в интервале температур 298-318К свидетельствует об эндотермическом характере образования поликомплекса в указанном интервале. Изменения значений энтропии связаны с разрушением сольватных оболочек лигандных групп ПЭГ и иона меди, вытеснением молекул растворителя и образованием хелатных структур. Методом ИК-спектроскопии установлено, что атомы кислорода полимерного лиганда принимают участие в образовании координационной связи с ионом металла-комплексообразователя.*

Ключевые слова: *полимерметаллический комплекс, ионы меди(II), полиэтиленгликоль, термодинамические характеристики, устойчивость*

Introduction

The interest in studies of polymer-salt complexes formed in solutions and films between metal ions and water-soluble polymers is due to the wide possibilities of their practical use: for example, for the extraction and concentration of rare and noble metals, for the creation of highly effective polymer catalysts (in the reaction of vanillin production from lignin use as a catalyst a polymer-metal complex based on copper chloride and polyethylene glycol), semipermeable membranes, water treatment, for synthesis complex oxide materials, etc. [1,2].

The properties of such systems are largely determined by the interaction between the ion and the polymer in aqueous solutions, which includes the hydration of polymer ions and macromolecules, complexation, and electrostatic interactions. Such a basic characteristic of the interaction of metal ions with polymers as a complexation constant, which, according to the basic principles of physical chemistry [3], associated with the standard change in Gibbs' energy during the reaction.

This value is integral in nature and depends on changes in both enthalpy and entropy during binding. The enthalpy and entropy contributions to the Gibbs' energy of complexation are usually not specially evaluated. Even for low molecular weight complexes, such data are rare [4]. Meanwhile, for 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. Mixes of copper ions with poly(ethylene glycol) (PEG) are used and tested for various application: for drug delivery systems [5]; for tumor targeting [6, 7]; for copper electrodeposition for on-chip metallization [8]; for preparation of copper nanoparticles [9].

The aim of this work was to study the complexation process between a water-soluble polymer - polyethylene glycol and copper(II) chloride, using widespread electrochemical methods (potentiometry, conductometry) and the calculated modified Bierrum's method.

Experimental part

Copper(II) chloride ($CuCl_2$ $2H_2O$), polyethylene glycol (molecular mass 10000, Aldrich), distilled water, nitric acid (HNO_3) acid were used without purification. Processes of complexing of copper(II) ions with PEG were investigated by potentiometric and conductometric methods. Potentiometric measurements were conducted on ionomer pX-150MI with using silver chloride and glass electrodes. Conductometric studies were performed on a device Conductivity Meter 13701/93 (PHYWE, Germany) in thermostated conditions. All experiments have been carried out under temperature control with an accuracy of pH ± 2. FT–IR spectra of PEG and the Cu-PEG complex were recorded on the FT IR-4100 type A JASCO device in the range of 4000-450 cm-1. FT-IR-spectra were taken in analytical laboratory at the Technical University of Kaiserslautern (TUK, Germany).

Synthesis of the $CuCl_2$-PEG complex was carried out as follows. The salt $CuCl_2$ $2H_2O$ (3.409 g, 0.02 mol) and PEG polymer (2.48 g, 0.04 mol) were placed in 50 ml round-bottom flask and dissolved in 10 ml of distilled waters. The obtained mix was stirredduring1 hour before the complete linking of polymer with Cu(II) ions at ambient temperature. The synthesized complex of green color was dried and stored on air at ambient temperature. Yield: 2.67g (60%).

Results and discussion

One of the informative methods for studying the complexation process in the polymer ligand – metal ion system is the pH-potentiometric titration method. Figure 1 shows the curve of potentiometric titration of an aqueous solution of polyethyleneglycol with Cu^{2+} ions. As can be seen from Figure 1, the interaction of the reagents is accompanied by a decrease in the pH of the solution, which is probably due to the formation of a donor–acceptor bond of the polyligand with copper ions. From the titration curve, the optimal molar ratio of reacting components k (k = [Men+]/[PEG]) was found.

Experimental data indicate the formation of a polymer-metal complex with an optimal molar ratio of components $k=[Cu^{2+}]/[PEG] = 0.50$. This means that two composite mono link of polyethyleneglycol accounts for one metal ion which complexing agent [1].

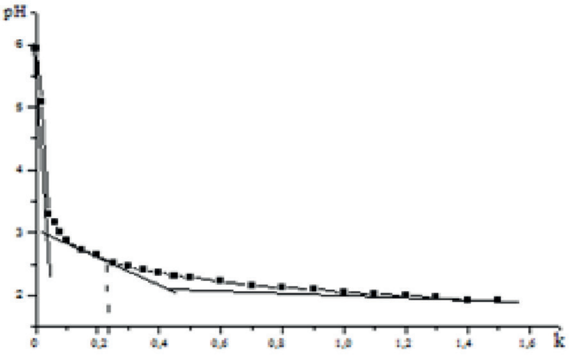

Figure 1 – Curve of potentiometric titration of PEG (10-2 M) by copper(II) chloride solution (10-2 M)
$k = [Cu^{2+}]/[PEG]$

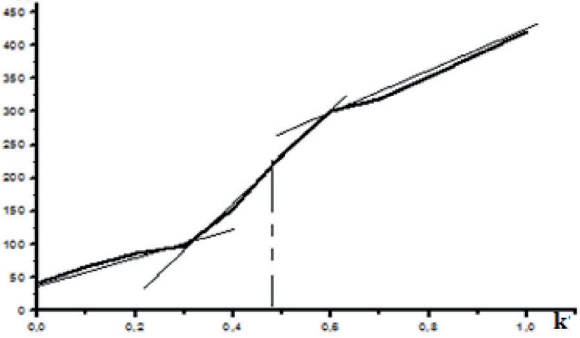

Figure 2 – Curve of conductometric titration of PEG(10-2 M) by copper(II) chloride solution(10-2 M)
$k = [Cu^{2+}]/[PEG]$

To confirm the composition of the obtained compound, the dependence of the electrical conductivity on the ratio of the initial components of the system was studied (Figure 2). The increase in electrical conductivity is due to the released H^+ ions during the reaction between the d-element ions and ligand macromolecules. As can be seen from Figure 2, the electric conductivity of the solution with an increase in the molar content of metal ions passes through the inflection point at the ratio PEG–Cu^{2+} = 2:1. It should be noted that the results of pH-potentiometric titration correlate with the data of conductometric studies.

A comprehensive study of the characteristics of the formation of polymer – metal complexes, i.e. determination of the stability constants, structure and composition of complexes, the disclosure of the mechanism of their formation is of great theoretical interest. Therefore, the work presents the results obtained by the modified Bierrum's method. For this aim, the PEG solution was titrated with nitric acid in the presence and absence of metal ions - a complexing agent in the temperature range 298–313 K at ionic strengths of the solution I = 0.1–0.2 mol/L, where $NaNO_3$ was used as an indifferent electrolyte (turbidity of solution was observed when using sodium chloride as an indifferent electrolyte).

Sodium salt, dissolved in an aqueous solution, reacted with the polar groups (hydroxyl groups in PEG) of the polymer unit, with the formation of interblock bridging. The appearance of this kind of connection complicates the movement of the chains, which leads to an increase in the time reaching the equilibrium state. If the bond formed is strong, then the dissolution of the polymer is complicated [10, 11].

Figure 3 shows the pH-potentiometric titration curves at T=298 K, I=0.10 mol/L (the potentiometric titration curves for other values of temperature and ionic strength have a similar form).As can be seen from Figure 3, the titration curves in the presence of metal ions of the complexing agent are in a more acidic region than in their absence, which indicates the complexation process between the polymer ligand and the metal ion [12, 13].

To interpret the displacement of the titration curves, the modified Bierrum's method was used. The calculated data performed using it are presented in Table 1. The calculated data also confirm the formation of polymer-metal complex with the composition [Me]:[L] = 1:2 in the PEG–Cu^{2+} system. As can be seen from Table 1, the complexing metal ion and the polymer ligand form two coordination bonds with each other, which is consistent with the results of experimental studies. With an increase in the concentration of nitric acid, the bond O----Me^{2+}weakens.

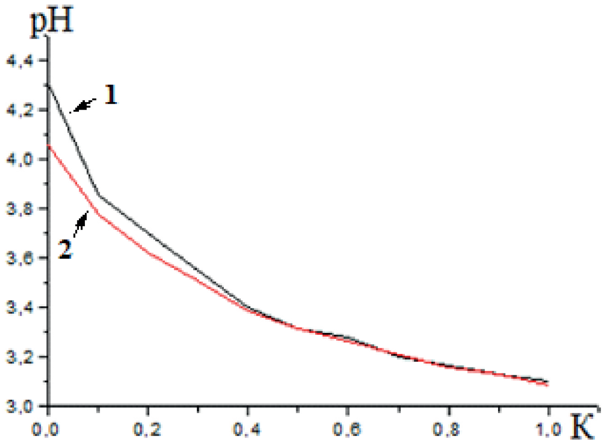

Figure 3 – Curves of potentiometric titration of aqueous solutions PEG–Cu2+ by nitric acid (10-2) at T=298 K, I=0,1 mol/L

(1 – a curve of potentiometric titration in absence of a metal ion,
2 – a curve of potentiometric titration in the presence of a metal ion)

This is explained by the process of protonation of the functional group of the polymer, since the O----Me^{2+}bond is weaker than O----H+ [14].

It is known that transition metal ions, when interacting with polymers, may not realize their maximum coordination number, since the ions of these metals can be coordinatively saturated due to acid anions or solvent molecules[15].In turn, steric repulsion between large ligands and electrostatic mutual repulsion of anions - ligands when they are replaced by water molecules from a positively charged metal ion can also inhibit the coordination of additional ligands [16].

Table 1 – Values of Bjerrum's formation functions of the PEG-Cu^{2+} complex at 298K and I = 0.1 mol/L

pH	[LH+]×104, mol/La	[L]×104, mol/Lb	[LC] ×103, mol/Lc	pLd	ne
3,97	2,26	13,49	1,76	2,87	1,13
3,89	5,37	16,22	1,17	2,79	0,75
3,79	8,37	10,72	1,42	2,97	0,91
3,73	11,46	8,91	1,29	3,05	0,83
3,68	14,56	7,24	1,15	3,14	0,74
3,63	17,64	5,89	0,98	3,23	0,63
3,59	20,74	4,90	0,77	3,31	0,49
3,57	23,95	4,79	0,46	3,32	0,29
3,53	27,02	3,80	0,25	3,42	0,16
3,48	29,99	2,75	0,05	3,56	0,04

^{a}[LH^{+}] – concentration of the protonated ligand groups;
^{b}[L] – concentration of the free ligands which are not involved in a complexing process;
^{c}[L]$_{C}$ – concentration of the ligand groups connected in a complex;
^{d} pL or -lg[L] – concentration of the free ligands calculated on Henserson-Hasselbach equation pH = pK$_{\alpha}$+ mlg[L]/[LH^{+}], where m - the empirical coefficient considering interlink interaction of a polymeric chain;
^{e}n – Bjerrum's formation functions or average number of bound ligands in a solution of a certain composition with one metal atom.

For a more detailed understanding of the complexation processes of high molecular ligands with metal ions, it is necessary to calculate the observed changes in important thermodynamic parameters such as the Gibbs' energy, enthalpy, and entropy of these processes. Since systems involving high molecular weight compounds are complex, the authors of a number of works [17, 18] it was suggested that the classical laws of thermodynamics can be applied to systems with polymer ligands. The stability of the complex is determined by the equilibrium constant of its formation. The latter is a measure of the released heat and the change in entropy during the reaction. As can be seen from Table 2, the values of the stability constants of the polymer-metal complex of copper (II) ion with PEG increases with elevating temperature, so can be assumed the complexation process is endothermic. The possibility of the occurrence of the complexation reaction in these systems in the forward direction is confirmed by the negative sign of the Gibbs' energy of the investigated processes.

Table 2 –Thermodynamic characteristics of formation process of the PEG–Cu^{2+} complex in an aqueous solution

T, K	lgβ^{0a}	-ΔrG0, kJ/mol^{b}	ΔrH0, kJ/mol^{c}	ΔrS J/mol.K^{d}
298	5,98±0,06	34,11±0,42	117,30±0,11	501,05±0,15
308	6,10±0,07	35,98±0,41		
318	7,25±0,09	44,13±0,45		

aβ^{0} – reference thermodynamic constant of complexes stability;
b ΔrG0 – Gibbs's energy change of reaction;
c ΔrH0 – enthalpy change of reaction (heat effect);
d ΔrS0– entropy change of reaction.

The complexation process of Cu^{2+} ions is characterized by a positive enthalpy, i.e., the interaction of the central ion with the polymer ligand is accompanied by heat absorption [19]. The sign of $\Delta_r H$ does not favor the spontaneous course of the process. Thus, complexation in this system is ensured by a strong increase in the entropy of the system. The process of binding of ions to polymer functional groups leads to a limitation of ion mobility, is entropically disadvantageous, and contributes to a decrease in entropy. The reaction between copper ions and polyethyleneglycol is characterized by a positive value of entropy.

This fact can be explained by two reasons: it can be assumed that the positive $\Delta_r S$ for the system under study is due to the dehydration of the ion and the functional group acting as a ligand. In this case, the released water molecules acquire translational mobility, resulting in increased entropy. An increase in the mobility of water molecules in the structure of polymer-salt solutions was previously detected by dielectric relaxation [20].

Another possible reason for the large positive value of entropy may be the chelate effect during complexation, when one ion binds to several functional groups. For low molecular weight systems, it was 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 a complexing ion by functional groups belonging to one ligand molecule is entropically beneficial, since more water molecules are released during dehydration than ligand molecules bind [21].

The Fourier transform infrared spectra of PEG and PEG–$CuCl_2$ complex were shown in Figure 4. The bands due to 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. Also, the aliphatic C–H stretching, in 1464and 1353 cm^{-1} were due to C–H bending vibrations [22]. The broad peak in 539 cm^{-1} related to $CuCl_2$ banding with oxygen from hydroxylgroups of PEG chains. Therefore, the FT-IR spectra showed the existence of 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). It is known that the polymer ligand PEG, due to the presence in its chain of an oxygen atom – an electron donor, is able to form complexes with transition metal ions having vacant orbitals, in particular with Cu (II) ions [23].

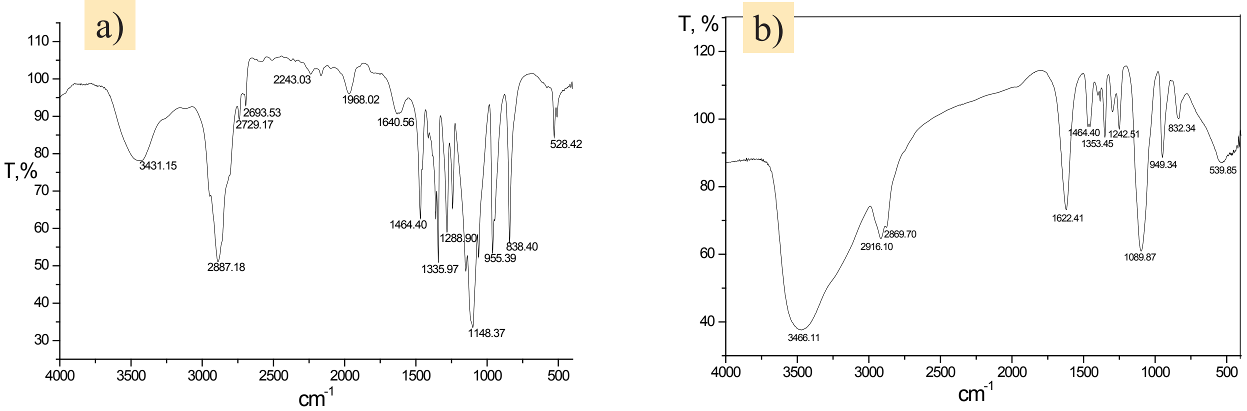

Figure 4 – Fourier transform infrared spectraof PVP (a) and complex [Cu(PEG)2]Cl_2 *(b)*

The schematic illustration of the synthesis of complex PEG–$CuCl_2$ is depicted schematically in Figure 5. As shown the complexation of copper ions occur due to the presence of van der waals forces between the oxygen negatively charged groups present in the molecular structure of the PEG.

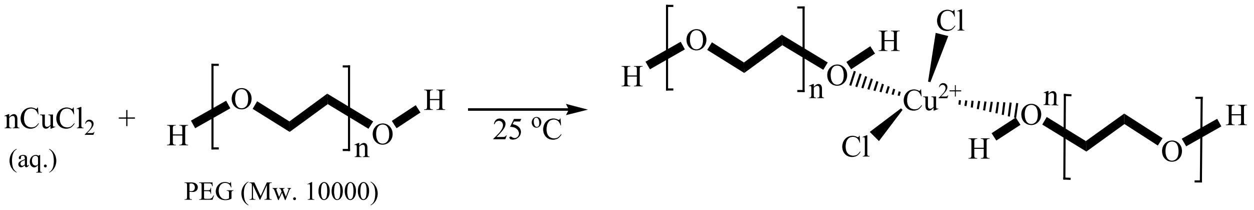

Figure 5 – Schematic illustration showing the interactions between the hydroxyl groups in polyethylene glycol (PEG) with the dissolved in water copper(II) chloride

The mechanism of interaction of copper ions with PEG is far from well-understanding and the following models were suggested: formation of Cu-Cl-PEG bridge [24,25], formation of PEG-$Cu^+(Cu^{2+})$-Cl^- [26] or Cu-ion which is coordinated by two oxygen atoms of PEG and by one chlorine ion [27].

In summary, we have described a simple method to synthesize polymer-metal complex based on copper(II) chloride and polyethylene glycol. Using potentiometric and conductometric titration, the structure of the polymeric complex was established and stability constants were calculated. Experimental data indicate the formation of a polymer-metal complex with an optimal molar ratio of components $k=[Cu^{2+}]/[PEG] = 0.50$, whose stability depends on the ionic strength of the solution, temperature. Methods of an IR-spectroscopy confirmed coordination of a polymeric ligand of PEG in a complex. It was established that atoms of oxygen of polymeric ligands share in formation of a coordination bond with a metal ion. Thermodynamic characteristics indicate the potential for the process under study in the direction of formation of the polymer-metal complex.

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