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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

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STUDYING THE COMPOSITION OF COMPLEXES ON THE BASIS OF PALLADIUM(II), COPPER(II), IRON(III) CHLORIDES AND POLYVINYLPYRROLIDONE

Abstract. The compositions of polymer-metal complexes based on palladium(II), copper(II), iron(III) chlorides and polyvinylpyrrolidone were established by potentiometric and conductometric methods. The values of the Bjerrum formation functions were calculated. According to the experimental data obtained for determination the composition of the complex, titration curves were constructed and the optimal molar ratios of the reacting components were found. The obtained calculated data indicate the formation of polymeric complexes of palladium and copper, in which one complex-metal ion forms into three compound mono-link of polyvinylpyrrolidone. And in the case of the iron polymeric complex, there is one ion of the complexing metal for the four constituent mono-link of polyvinylpyrrolidone. Coordination saturation of metal complexing agents in these complexes is due to solvent molecules or anion of metal salts. The structure and morphology of the synthesized complexes were studied using IR- spectroscopy and scanning electron microscopy. It has been established that the oxygen atoms of polymeric ligands take part in the formation of a coordination bond with the metal ion. The results of electron microscopy indicate the formation of polymer films of a complex with a porous inhomogeneous amorphous structure.

Key words. Polyvinylpyrrolidone, palladium, copper, iron, complexation, Bjerrum method, stability constants, composition, thermodynamics.

Introduction

Coordination compounds are widely used as homogeneous and heterogeneous supported catalysts. Chemical transformations in the presence of coordination compounds underlie many catalytic processes. It is known that they are able to activate molecules of alkenes, alkynes, carbon monoxide, oxygen, which opens up broad opportunities for the development of new catalytic processes [1].

An additional impetus for the development of catalysis by complexes was the general tendency to create milder reaction conditions. Classical processes using heterogeneous metal oxide or metal catalysts are sometimes called “expensive” processes, bearing in mind the high costs per ton of product produced. These costs are determined by high temperatures and pressures at a fairly low, as a consequence, the selectivity of the process. In addition, relatively low degrees of conversion of the starting materials often lead to the need to separate the reaction product from highly diluted mixtures, as well as the recycle of unreacted reagent. Polymer-metal complexes used as homogeneous catalysts, on the contrary, usually operate at low temperatures and pressures with high efficiency and selectivity for the reaction products [2].

The aim of this work is to study the process of complexation of polyvinylpyrrolidone (PVP) with Pd^{2+}, Cu^{2+}, Fe^{3+} ions.

Experimental part

Palladium(II) chloride $PdCl_2$, copper(II) chloride $CuCl_2 \cdot 2H_2O$, iron(III) chloride $FeCl_3 \cdot 6H_2O$, polyvinylpyrrolidone (molecular weight 40,000, AppliChem, Germany), hydrochloric acid, sodium hydroxide, sodium chloride were used without prior purification.

The processes of complexation of palladium(II), copper(II) and iron(III) ions with PVP were investigated by potentiometric and conductometric methods [3]. Potentiometric studies were carried out in thermostated conditions on the pX-150MI ionomer using silver chloride and glass electrodes. The pH measurement accuracy was 0.02 pH units. Conductometric studies were performed on a ConductivityMeter 13701/93 device (PHYWE) under thermostatically controlled conditions.

IR spectra of PVP and Pd(II)-PVP, Cu(II)-PVP and Fe(III)-PVP complexes were recorded on a FT IR-4100 type A JASCO instrument in the range of 4000–450 cm^{-1} at Kaiserslautern Technical University (TUK, Germany). SEM images were taken on a JSM-6490LA Jeol instrument equipped with an X-ray dispersive energy detector (EDX) for elementary analysis (JEOL, Japan). IR spectra and SEM images were obtained in analytical laboratories at the Technical University of Kaiserslautern (TUK, Germany). The stability constants of the PMC are calculated on the basis of the modified Bjerrum method [4].

Results and their discussion

In the works [5-7], the results on the determination of the compositions of polymer-metal complexes (PMC) based on PVP-$PdCl_2$, PVP-$CuCl_2 \cdot 2H_2O$, PVP- $FeCl_3 \cdot 6H_2O$ using potentiometric and conductometric titration were presented.

The reactivity of a chain molecule is largely determined by the chemical composition, configuration and conformation of the macromolecule, and knowledge of which makes it possible to determine the role and mechanism of the catalytic action of various functional groups of macromolecules that are part of the active centers [8]. The correctness of the final calculations depends on the theoretical laws and the accuracy of the source data. The calculations performed give results that should be consistent with the experimental data. In this connection, the modified Bjerrum method [9,10] was used to clarify the composition and determine the strength of the PMC. The polymer ligand solution was titrated with acid (HCl) or base (NaOH), depending on the nature of the complexing metal salt, with a change in the pH of the medium in the absence and presence of ions of the studied metals in the temperature range of 298–343 K (temperature selection due to the use of PMC as catalysts in the oxidation of octene–1 in an oxygen atmosphere [5]), with three values of the ionic strength of a solution of 0.1; 0.5; 1.0 mol/L (constants, determined for a given ionic strength, can be considered almost constant for solutions with ionic strength, which were taken when performing experiments. That is, for most calculations these values can be used without corrections for ionic strength [11] (sodium chloride was used as an indifferent electrolyte).

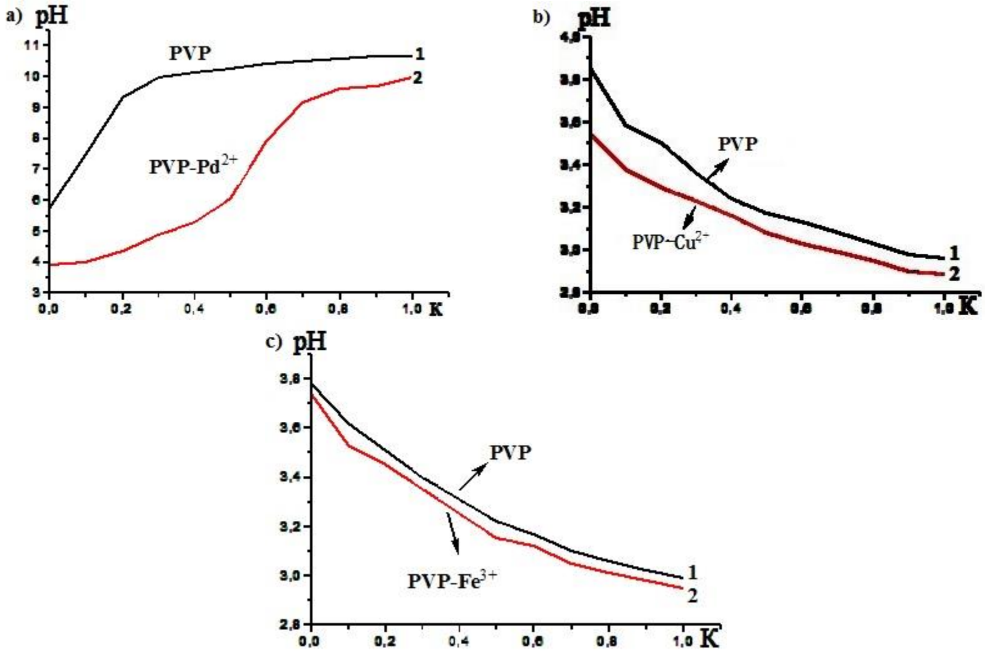

Figure 1 – Potentiometric titration curves of aqueous solutions of polyelectrolyte PVP (1a-c) and polymer–$PdCl_2$ (2a), polymer–$CuCl_2$ (2b) systems, polymer–$FeCl_3$ (2c) sodium hydroxide (curves 1a, 2a) and hydrochloric acid (curves 1b, 2b, 1c, 2c) at T = 298 K, I = 0.10 mol/L (where K is the optimal molar ratio of the reacting components [$Me^{2+/3+}$]/[PVP])

Figure 1 shows the curves of potentiometric titration of PVP with sodium hydroxide (1a, 2a) and hydrochloric acid (1b, 2b, 1c, 2c) in the absence and presence of Pd^{2+} (1a), Fe^{3+} (2b), Cu^{2+} (3b) ions at T = 298 K, I = 0.10 mol/L (potentiometric titration curves for other values of temperature and ionic strength have a similar appearance).

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

A modified Bjerrum method was used to interpret the bias of the titration curves. The obtained data, performed with its use, are presented in Table 1.

Table 1 – The calculated values of the Bjerrum's formation functions of PVP–$PdCl_2$, PVP–$CuCl_2$, PVP–$FeCl_3$ systems (T = 298K, I = 0.10 mol/L)

System	$[LH^+]$, mol/L [a]	[L]. mol/L [b]	$[L_C]$, mol/L [c]	pL[d]	n[e]
PVP – Pd^{2+}	$2,48 \cdot 10^{-4}$	$0,01 \cdot 10^{-5}$	$3,08 \cdot 10^{-3}$	6,89	2,99
	$6,01 \cdot 10^{-4}$	$0,04 \cdot 10^{-5}$	$2,73 \cdot 10^{-3}$	6,39	2,65
	$9,49 \cdot 10^{-4}$	$0,09 \cdot 10^{-5}$	$2,38 \cdot 10^{-3}$	6,09	2,31
	$13,00 \cdot 10^{-4}$	$0,15 \cdot 10^{-5}$	$2,03 \cdot 10^{-3}$	5,83	1,97
	$16,40 \cdot 10^{-4}$	$0,26 \cdot 10^{-5}$	$1,69 \cdot 10^{-3}$	5,59	1,64
	$19,80 \cdot 10^{-4}$	$0,44 \cdot 10^{-5}$	$1,35 \cdot 10^{-3}$	5,36	1,31
	$23,20 \cdot 10^{-4}$	$0,78 \cdot 10^{-5}$	$1,00 \cdot 10^{-3}$	5,11	0,97
	$26,60 \cdot 10^{-4}$	$1,20 \cdot 10^{-5}$	$0,66 \cdot 10^{-3}$	4,92	0,31
PVP - Cu^{2+}	$0,99 \cdot 10^{-4}$	$3,46 \cdot 10^{-1}$	$9,00 \cdot 10^{-4}$	0,46	2,7
	$1,99 \cdot 10^{-4}$	$2,81 \cdot 10^{-1}$	$8,01 \cdot 10^{-4}$	0,55	2,4
	$2,99 \cdot 10^{-4}$	$0,76 \cdot 10^{-1}$	$7,02 \cdot 10^{-4}$	1,12	2,1
	$3,97 \cdot 10^{-4}$	$0,69 \cdot 10^{-1}$	$6,03 \cdot 10^{-4}$	1,16	1,8
	$4,97 \cdot 10^{-4}$	$0,71 \cdot 10^{-1}$	$5,03 \cdot 10^{-4}$	1,15	1,5
	$5,96 \cdot 10^{-4}$	$0,68 \cdot 10^{-1}$	$4,03 \cdot 10^{-4}$	1,17	1,2
PVP – Fe^{3+}	$0,64 \cdot 10^{-3}$	$1,07 \cdot 10^{-3}$	$11,6 \cdot 10^{-3}$	2,97	1,34
	$1,52 \cdot 10^{-3}$	$1,51 \cdot 10^{-3}$	$10,3 \cdot 10^{-3}$	2,82	1,19
	$2,36 \cdot 10^{-3}$	$1,44 \cdot 10^{-3}$	$9,50 \cdot 10^{-3}$	2,84	1,10
	$3,42 \cdot 10^{-3}$	$1,58 \cdot 10^{-3}$	$8,30 \cdot 10^{-3}$	2,80	0,96
	$4,18 \cdot 10^{-3}$	$1,20 \cdot 10^{-3}$	$7,90 \cdot 10^{-3}$	2,92	0,91
	$5,21 \cdot 10^{-3}$	$1,17 \cdot 10^{-3}$	$6,90 \cdot 10^{-3}$	2,93	0,80
	$6,38 \cdot 10^{-3}$	$1,23 \cdot 10^{-3}$	$5,70 \cdot 10^{-3}$	2,91	0,66

Not: [a] $[LH^+]$ – concentration of the protonated ligand groups; [b] [LH+] – 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 = 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 calculated data confirm the formation of PMC with the composition [Me]:[L] = 1:3 in the PVP–Pd^{2+}, PVP–Cu^{2+} systems, and with the composition [Me]:[L] = 1:4 in the PVP–Fe^{3+} system. 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 coordinated to saturate with anionic acids or solvent molecules [12]. In turn, steric repulsion between large ligands in volume and electrostatic mutual repulsion of anion ligands when they are replaced by water molecules at a positively charged metal ion can also inhibit the coordination of additional ligands [13].

For a more detailed understanding of the complexation of high-molecular-weight ligands with metal ions, it is necessary to calculate the changes observed in this important thermodynamic parameters, such as Gibbs' energy, enthalpy and entropy of these processes. Since systems involving high-molecular compounds are complex, in this connection, the authors of a number of papers [14,15] suggested that the classical laws of thermodynamics can also be applied to systems with polymeric ligands.

From table 2 it follows that the most stable complex is PMC based on PVP and iron(III) chloride. This fact is due to the following factors: first, the complex formation reaction can be explained using the theory of acids and Lewis bases. According to the Lewis theory, acids are ions or compounds that accept a pair of electrons, i.e. such particles are electron acceptors. Thus, metal ions can be considered as polybasic acids with a deficiency of electronic pairs, corresponding to the maximum coordination number, which form bonds with bases. Secondly, the strength of the acid increases with increasing valence (in the systems under consideration, palladium and copper are in the bivalent state, and iron in the trivalent state). It is also known that metal ions are divided into three large groups: the first group is alkaline and alkaline-earth elements; the second group – transition metals with d^{10}- or d^8-electron configuration (Pd^{2+}, Cu^{2+}), which are more inclined to form stable complexes with ligands through sulfur, arsenic, phosphorus atoms; the third, largest group includes transition metal ions with partially filled d-orbitals.

Ions of metals of this group, first of all, form complexes with nitrogen and oxygen-containing ligands. According to Pearson's theory [16], Pd^{2+}, Cu^{2+} ions are soft acids, while the Fe^{3+} ion is a hard acid, and the oxygen atom is a hard base. The most stable complexes are formed by the interaction of hard acids and bases, on the one hand, and soft acids and bases, on the other one. From this it follows that among the represented metals, iron ions have a high affinity for oxygen [17].

Calculation of thermodynamic parameters showed that the complex formation of PVP with Pd^{2+}, Cu^{2+}, Fe^{3+} ions is characterized by negative values of Gibbs' energy, which indicates a spontaneous process of PMC formation in these systems (Table 2). The following pattern is observed for the Pd^{2+}–PVP complex: a positive value of the change in enthalpy ($\Delta_r H^0$) in the temperature range 298–318 K indicates the endothermic nature of polycomplex formation, therefore, with an increase in temperature in the specified interval, the stability of the latter increases. And in the temperature range 318-343K, the complexation process is accompanied by the release of heat (an exothermic process), as a result of which the strength of the polymer-metal complex decreases with increasing temperature. The obtained fact of the ambiguous effect of temperature on the complexation process is probably due to conformational changes in the structure of the polymer-polyvinylpyrrolidone as shown in [18]. The authors found that the conformational changes of PVP in an aqueous medium are accompanied by exoeffects, the values of which depend on the temperature and molecular weight of the polymer.

The complexation reactions of copper and iron ions with PVP are accompanied by exoeffects, as indicated by negative enthalpy values. With an increase in temperature in the temperature range of 298–318 K, the stability of PMC decreases.

Complexation processes in binary PVP–Pd^{2+} and PVP–Cu^{2+} systems are characterized by positive entropy values, which is caused by the destruction of the hydration shells of PVP ligand groups and the displacement of water molecules from the first coordination sphere of metal ions. The formation of iron complexes with PVP is characterized by negative values of entropy change. Negative entropy change ΔS with a negative enthalpy change ΔH indicates that the reaction under study is possible at sufficiently low temperatures and the linear dependence of Δ on ΔS is described by the equation $\Delta H = -0.36\Delta S + \text{const}$, which indicates donor-acceptor interaction [8].

Table 2 – Thermodynamic characteristics of the complexation of Pd^{2+}, Fe^{3+}, Cu^{2+} ions with PVP

System	T, K	$\lg\beta^0$	$-\Delta_r G$, kJ/mol	$\pm\Delta_r H$, kJ/mol	$\pm\Delta_r S$, J/(mol·K)
PVP – Pd^{2+}	298	9,10±0,08	56,94±0,62	1288,4±0,10	4541,7±0,15
	318	14,20±0,20	109,17±0,69		
	343	11,20±0,09	81,10±0,60	898,5±0,12	2335,3±0,12
PVP – Cu^{2+}	298	14,5±0,19	82,719±0,09	175,7±0,30	218,621±0,94
	308	14,4±0,18	84,906±0,11	487,5±0,80	1307,13±0,57
	318	11,50±0,25	71,834±0,08	244,9±0,90	544,255±0,30
PVP – Fe^{3+}	298	31,00 ± 0,01	176,849 ± 0,01	725,653±0,01	1841,620±0,01
	318	23,00 ± 0,03	140,016±0,04	174,334±0,01	5041,910±0,02
	343	10,10± 0,02	64,397±0,05	1134,375±0,01	3213,150±0,06

The nature of the modifying effect of PVP on Pd(II), Cu(II), Fe(III) ions and the possible molecular structure of the PVP-$PdCl_2$, PVP-$CuCl_2$, PVP-$FeCl_3$ complexes was studied using IR spectroscopy (Figure 2). As can be seen from the IR spectra, 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 Pd(II), Cu(II), Fe(III) in the complexes PVP-$PdCl_2$, PVP-$CuCl_2$, PVP-$FeCl_3$. The IR spectra of the complexes under study contain a band at 3400 cm^{-1}, characteristic of PVP. The carbonyl group in PVP is characterized by a peak at 1651 cm^{-1}, extended due to the C=N bond in the lactam ring. This band shifts to 1510–1645 cm^{-1} in the studied complexes. Differences in the IR spectra of PVP and PVP-$PdCl_2$, PVP-$CuCl_2$, PVP-$FeCl_3$ complexes are observed as a result of donor-acceptor interaction between the oxygen atom in the polymeric ligand PVP and metal ions – complexing agents [18-20].

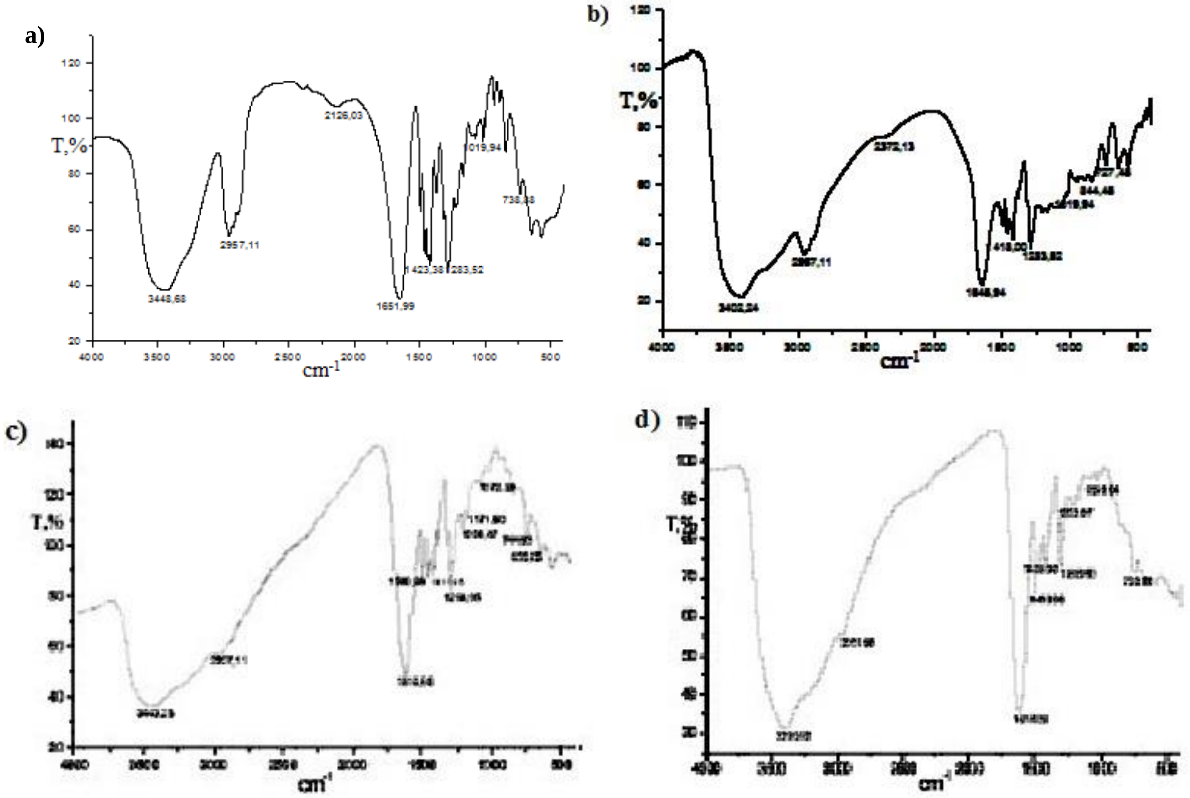

Figure 2 – IR spectra of PVP (**a**) and complexes of $[Pd(PVP)_3Cl_2]$ (**b**), $[Cu(PVP)_3Cl_2]$ (**c**), $[Fe(ПВП)_4(H_2O)_2Cl_3]$ (**d**)

To study the surface of polymer-metal complexes, the method of scanning electron microscopy was used (Figure 3). Analysis of micrographs indicates the formation of polymer films with a porous inhomogeneous amorphous structure.

Conclusion

Thus, the composition of the PMC was defined by modifying method of Bjerrum. The coordination of the polymer ligand of PVP in the complexes was confirmed by IR spectroscopy and scanning electron microscopy. The morphology and peculiarities of their surface were studied. It has been established that the oxygen atoms of polymeric ligands participate in the formation of a coordination bond with metal ions of complexing agents. Electron microscopy results indicate the amorphous structure of the complexes. The thermodynamic parameters of the PMC were calculated, which indicate the process of complexation between metal ions and the polymer ligand.

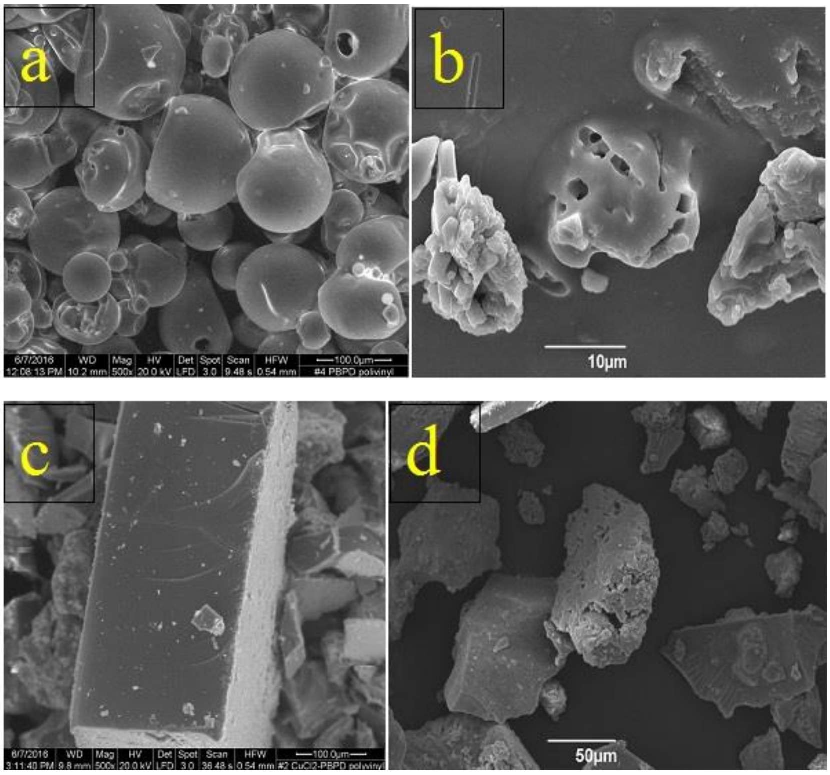

Figure 3 – SEM images of PVP (**a**) and complexes PVP-PdCl$_2$ (**b**),
PVP-CuCl$_2$ (**c**), PVP-FeCl$_3$ (**d**)

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ПАЛЛАДИЙ(II), МЫС(II), ТЕМІР(III) ХЛОРИДТЕРІ ЖӘНЕ ПОЛИВИНИЛПИРРОЛИДОН НЕГІЗІНДЕГІ КЕШЕНДІ ҚОСЫЛЫСТАРДЫҢ ҚҰРАМЫН ЗЕРТТЕУ

Аннотация. Палладий(II), мыс(II), темір(III) хлоридтері және поливинилпирролидон негізіндегі полимерметалдық кешенді қосылыстардың құрамы потенциометрлік және кондуктометрлік әдістермен анықталған. Бьеррумның түзілу функциясы мәндері есептелген. Алынған тәжірибиелік мәліметтерге сүйене отырып, титрлеу қисықтары тұрғызылып, әрекеттесуші құраушылардың оптималды мольдік қатынастары табылған. Есептеу нәтижесінде алынған мәліметтер палладий және мыс кешенді қосылыстарының түзілгендігін дәлелдейді, ондағы поливинилпирролидонның үш буынына бір металл–кешентүзгіш ионы келеді. Ал темірдің полимерлі кешенді қосылысында поливинилпирролидонның төрт буынына бір металл–кешентүзгіш ионы сәйкес келеді. Металл – кешентүзгіш иондарында координациялық қанығу үдерісі еріткіш молекуласы немесе металл тұздары аниондары есебінен жүзеге асады. ИҚ–спектроскопия және сканирлеуші электрондық микроскопия (СЭМ) әдістері көмегімен синтезделген кешенді қосылыстардың құрылысы және морфологиясы зерттелген. Полимерлі лигандтағы оттегі атомы металл – кешентүзгіш ионымен координациялық байланыс түзуге қатысатындығы дәлелденген. Электрондық микроскопия нәтижесі кеуекті біртекті емес аморфты құрылымға ие кешенді қосылыстың полимерлі қабықшасының түзілетіндігін көрсетеді.

Түйін сөздер. Поливинилпирролидон, палладий, мыс, темір, кешентүзілу, Бьеррум әдісі, тұрақтылық константасы, құрамы, термодинамика.

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ИЗУЧЕНИЕ СОСТАВА КОМПЛЕКСОВ НА ОСНОВЕ ХЛОРИДОВ ПАЛЛАДИЯ(II), МЕДИ(II), ЖЕЛЕЗА(III) И ПОЛИВИНИЛПИРРОЛИДОНА

Аннотация. Составы полимерметаллических комплексов на основе хлоридов палладия(II), меди(II), железа(III) и поливинилпирролидона были установлены потенциометрическим и кондуктометрическим методами. Были рассчитаны функции образования Бьеррума. По полученным экспериментальным данным по определению состава комплекса были построены кривые титрования и найдены оптимальные мольные соотношения реагирующих компонентов. Полученные рассчитанные данные свидетельствуют об образовании полимерных комплексов палладия и меди, в которых на три составных монозвена поливинилпирролидона приходится один ион металла-комплексообразователя. А в случае полимерного комплекса железа на четыре составных монозвена поливинилпирролидона приходится один ион металла-комплексообразователя. Координационная насыщенность металлов-комплексообразователей в этих комплексах осуществляется за счет молекул растворителя или аниона солей металлов. Методами ИК-спектроскопии и сканирующей электронной микроскопии (СЭМ) исследованы строение и морфология синтезированных комплексов. Установлено, что атомы кислорода полимерных лигандов принимают участие в образовании координационной связи с ионом металла-комплексообразователя. Результаты электронной микроскопии указывают на образование полимерных плёнок комплекса с пористой неоднородной аморфной структурой.

Ключевые слова: поливинилпирролидон, палладий, медь, железо, комплексообразование, метод Бьеррума, константы устойчивости, состав, термодинамика.

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