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Synthesis and study of structure of the iron chloride – polyvinylpyrrolidone complex

The polymer-metal complex on the basis of iron (III) chloride and a polyvinylpyrrolidone (PVP) was synthesized. The composition of this complex was established by potentiometric and conductometric methods. Titration curves were constructed and the optimum molar ratio of the reacting components was found ($k = [\text{Fe}^{3+}]/[\text{PVP}] = 0.24$). The obtained experimental data confirm formation of a polymeric complex of iron where one metal ion is bonded with four compound monolinks of a polyvinylpyrrolidone. Coordination saturation of metal ion in this complex is realized due to the molecules of solvent or anions of iron salt. On the basis of the modified Bjerrum's method constants of stability of a polymeric complex at various values of ionic strength of solution were calculated on which thermodynamic equilibrium constants of the studied processes were found. On the basis of thermodynamic constants of stability, using isotherm equations and isobars of Vant Hoff and Gibbs, changes of Gibbs' energy ($\Delta_r G^0$), enthalpy ($\Delta_r H^0$) and entropy ($\Delta_r S^0$) were calculated. Complexing reactions of iron ions with polyvinylpyrrolidone are accompanied by exo-effects what point to the negative values of an enthalpy change during reaction. The negative values of an entropy change ΔS at the negative change of an enthalpy ΔH indicated that the studied reaction is possible at rather low temperatures. It was established that oxygen atoms of polymeric ligands were involved in formation of a coordination bond with a metal ion. It was established that oxygen atoms of polymeric ligands took part in formation of a coordination bond with a metal ion. Using IR-spectroscopy and scanning electron microscopy a structure and morphology of the synthesized complex iron (III)chloride-polyvinylpyrrolidone were investigated. Results of electron microscopy indicate on formation of polymeric films of a complex with cellular nonuniform amorphous structure.

Keywords: polyvinylpyrrolidone, iron, complexing, Bjerrum's method, constant, stability, composition, thermodynamics.

Introduction

Iron (III) complexes are widely used as catalysts of many organic processes, because of the features of an electronic structure of iron in oxidized (d^5) and reduced (d^6) states, a possibility of regeneration by oxygen, high complexing ability and good solubility in organic solvents. Owing to interaction metal-ligand homogeneous catalysts on the basis of iron chloride (FeCl_3) have a high activity and selectivity in Michael reaction [1], allylation of aldehydes with allyltrimethylsilane [2], acetal-ene reaction [3], conversion of epoxides to acetonides [4], oxidative coupling reaction of 1,2-diarylethylene derivatives [5], synthesis of coumarins from phenols and β -ketoesters [6]. In turn, poly(N-vinyl-2-pyrrolidone) (PVP) is nontoxic, water-soluble and biologically compatible and therefore ecologically harmless polymeric ligand [7, 8]. It is stable against thermal degradation in solution and in relation to acids and salts. Due to ability to complexation, application of PVP as a ligand allows to obtain stable complexes with the transitional metals [9, 10]. In literature there are not numerous data on use of catalysts on the basis of iron (III) complexes with polymers and various branched ligands in oxidizing reactions [11–13]. It should be noted that according to literary and pa-

tent searching not enough attention is paid to studying of a composition and structure of the iron-polymer complexes used as catalysts.

In this work, results on establishment of regularities and the nature of interaction in aqueous solutions of iron (III) chloride with PVP, a number of physical and chemical methods as IR-spectroscopy, scanning electron microscopy, conductometry, potentiometry are presented.

Experimental

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), polyvinylpyrrolidone (molecular mass 40000, AppliChem, Germany), distilled water, hydrochloric acid were used without purification. Complexing processes of iron (III) ions with PVP were investigated by potentiometric and conductometric methods [14]. Potentiometric measurements were conducted on an ionomer pX-150MI with using silver chloride and glass electrodes. Conductometric studies were performed on a device ConductivityMeter 13701/93 (PHYWE, Germany) in thermostated conditions. All experiments have been carried out under temperature control with an accuracy of $\text{pH} \pm 2$. IR spectra of PVP and the Fe-PVP complex were recorded on the FT IR-4100 type A JASCO device in the range of $4000\text{--}450\text{ cm}^{-1}$. SEM images were produced on the device JSM-6490LA of Jeol. IR-spectra and SEM images were taken in analytical laboratories at the Technical University of Kaiserslautern (TUK, Germany).

Synthesis of the FeCl_3 -PVP complex was carried out as follows. The salt $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.70 g, 0.01 mol) and PVP polymer (4.44 g, 0.04 mol) were placed in 50 mL round-bottom flask and dissolved in 10 mL of distilled water. The obtained solution was mixed on a magnetic stirrer within 20–30 minutes before the complete linking of polymer with Fe (III) ions at ambient temperature. The synthesized complex of orange color was dried and stored on air at ambient temperature. Yield is 6.23 g (97 %).

Results and Discussion

Interaction between PVP and Fe^{3+} ions has been investigated by potentiometric and conductometric methods, which allowed establishing the structure, concentration and stability constants of the polymer/metal complex [15]. The high tendency to complexation, non-toxicity, good solubility in various solvents, including high solubility in aqueous mediums, provides to PVP broad application in textile, food, pharmaceutical industry and in medicine [16]. Curves of potentiometric and conductometric titration of PVP by iron (III) chloride are presented in Figures 1 and 2.

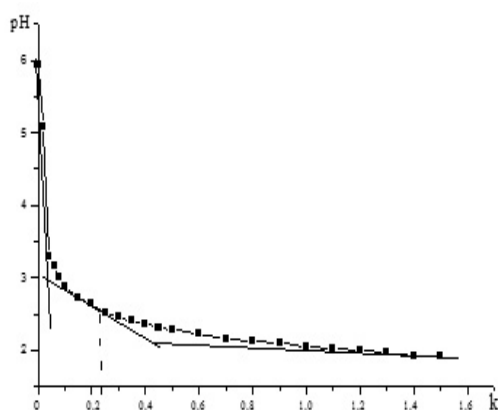


Figure 1. Curve of potentiometric titration of PVP (10^{-2} M) with iron chloride solution (10^{-2} M) $k = [\text{Fe}^{3+}]/[\text{PVP}]$

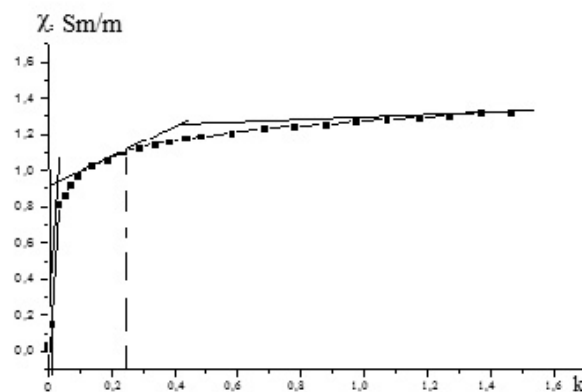
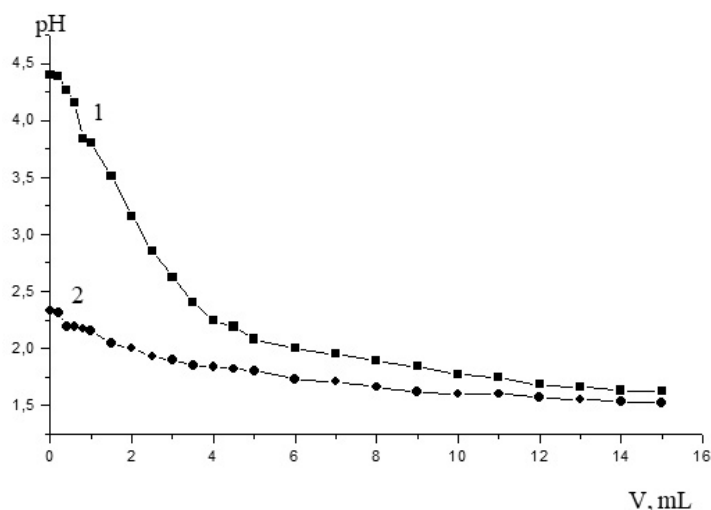


Figure 2. Curve of conductometric titration of PVP (10^{-2} M) with iron chloride solution (10^{-2} M) $k = [\text{Fe}^{3+}]/[\text{PVP}]$

Mixing of aqueous solution of polymer with solution of salt, apparently from Figures 1 and 2, is accompanied by pH decrease of medium that is explained by formation of protons of hydroxyl groups of the protonated PVP during complexing. The experimental data confirm formation of a polymer-metal complex with an optimum molar ratio of the components $k = [\text{Fe}^{3+}]/[\text{PVP}] = 0.24$. It means that one metal ion contacts with four compound mono-links of a polymeric ligand. Coordinative saturation of metal ion is probably realized at the expense of molecules of solvent or anion of iron salt. To confirm the composition of the formed

PVP-Fe³⁺ complex the dependence of a specific conductivity on a ratio of initial components of systems was investigated (Fig. 2). Increase of an electrical conductivity is caused by the allocated H⁺ ions during reaction between PVP with iron ions. The conducted conductometric studies indicate that a complexing process is followed by increase in an electrical conductivity of systems. In the course of complexing of a polymeric ligand PVP there is a decrease of its hydrodynamic sizes (chelate effect), allocation of protons that is confirmed by results of an experiment. According to the literary [17] and experimental data, it is possible to assume that in the studied PVP-Fe³⁺ system the complexes of composition [PVP]:[Fe³⁺] = 4:1 are formed (Fig. 1, 2).

In the Figure 3 curves of potentiometric titration of PVP solution by an aqueous solution of the hydrochloric acid in the absence and presence of a metal ion at $T = 318\text{ K}$, $I = 0.1\text{ mol/L}$ are presented. It is necessary to notice that curves of potentiometric titration at other values of temperature (298, 333 K) and ionic strength of solution ($I = 0.50$; 1.00) have a similar appearance. Curves of titration in the presence of metal ions as it is visible from the Figure 3, are in more acidic area, than in their absence that can demonstrate existence of a complexing process between a polymeric ligand and a metal ion. According to literary data [18, 19], the more shift of titration curves of systems polymer-metal ion of rather pure polymer, is higher stability of the polymer-metal complexes which are formed.



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

Figure 3. Curves of potentiometric titration of aqueous solutions PVP-Fe³⁺ by hydrochloric acid (10^{-2}) at $T = 318\text{ K}$, $I = 0.1\text{ mol/L}$

The calculated values of Bjerrum's formation functions of a polymer-metal complex on the basis of PVP and iron (III) chloride are presented in Table 1. Apparently from Table 1, the complexing ion of metal and a polymeric ligand among themselves form four coordination bonds that is agreed with results of the experimental studies. With increasing of the hydrochloric acid the bond O⁻-Me³⁺ is weakened. It is explained by protonation process of the functional group of polymer as bond O⁻-Me³⁺ is weaker than O⁻-H⁺ one [20].

Table 1

The calculated values of Bjerrum's formation functions of the PVP- Fe³⁺ complex
($T = 333\text{ K}$, $I = 0.50\text{ mol/L}$)

pH	[LH ⁺] mol/L	[L] mol/L	[L _K] mol/L	pL	n
3.60	0.85×10^{-3}	0.76×10^{-4}	3.24×10^{-2}	4.12	3.74
3.37	3.38×10^{-3}	2.95×10^{-4}	2.96×10^{-2}	3.53	3.41
3.20	5.91×10^{-3}	5.01×10^{-4}	2.99×10^{-2}	3.30	3.45
3.06	8.74×10^{-3}	7.24×10^{-4}	2.38×10^{-2}	3.14	2.75
2.90	12.1×10^{-3}	10.2×10^{-4}	2.02×10^{-2}	2.99	2.33
2.70	15.1×10^{-3}	12.6×10^{-4}	1.69×10^{-2}	2.90	1.95

On the basis of the modified Bjerrum's method constants of stability of a polymeric complex at various values of ionic strength of solution were calculated (0.10; 0.50; 1.00 mol/L) on which thermodynamic equilibrium constants of the studied processes (Table 2) were found. Stability of a complex is defined by the size of an equilibrium constant of its formation. The last is a measure of the emitted warmth and change of an entropy during reaction.

Apparently from Table 2, values of stability constants of a polymer-metal complex of an iron (III) ion with PVP with temperature increase decrease therefore it is possible to assume that a complexing process is the exothermic one. Consideration of an entropy is very important at formation of $[ML_6]^{n+}$ complex from $[M(H_2O)_6]^{n+}$. In such cases replacement of each subsequent molecule H_2O with a ligand L is at a loss more and more. In our case replacement of one molecule of water with each subsequent mono-link of PVP reduces by unit number of possible coordination places for the following mono-links of polymer. Besides, the more mono-links of molecule PVP in a complex, the probability of replacement of molecules of water with the subsequent polymeric ligand is less. Both of these factors reduce probability of formation, therefore, and stability of more high-replaced complexes. Other factors, such as steric repulsion between ligands larger on volume basis and a coulomb relative repulsion of ligands-anions at their replacement of molecules of water at a positively charged ion of metal, can also detain coordinating of additional ligands [21].

On the basis of results of conducted studies taking into account literary data it is possible to submit the following scheme of formation of a complex on the basis of iron(III) chloride and PVP (Fig. 4).

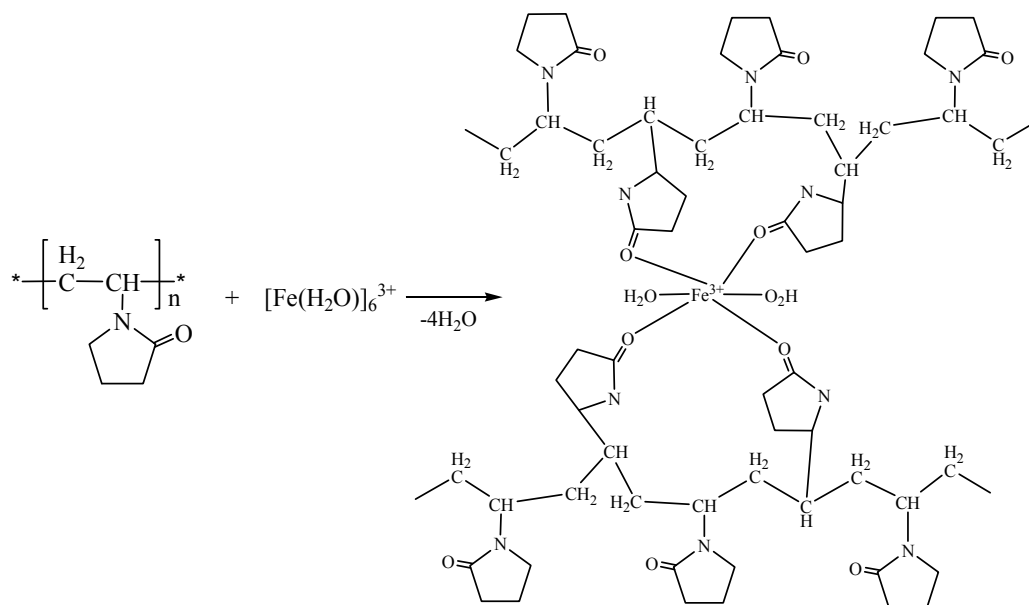


Figure 4. Scheme of formation of the PVP-iron(III) chloride complex

Table 2

Values of stability constants of the polymer-metal PVP- Fe^{3+} complex in an aqueous medium

T, K	I	$\lg\beta$
298	0	31.00
	0.1	21.45
	0.5	25.95
	1.0	32.51
318	0	23.00
	0.1	22.86
	0.5	28.50
	1.0	26.10
333	0	10.10
	0.1	14.00
	0.5	12.40
	1.0	13.40

It is known that knowledge of thermodynamic coordinates (changes of Gibbs energy ($\Delta_r G^0$), an enthalpy ($\Delta_r H^0$) and an entropy ($\Delta_r S^0$)) of studied processes is necessary for the scientifically based choice of optimum conditions of their carrying out in practice [22]. At the same time many researchers assume that for systems with participation of macromolecules the fundamental laws of thermodynamics established for the systems consisting of low-molecular weight compounds [23, 24] are used.

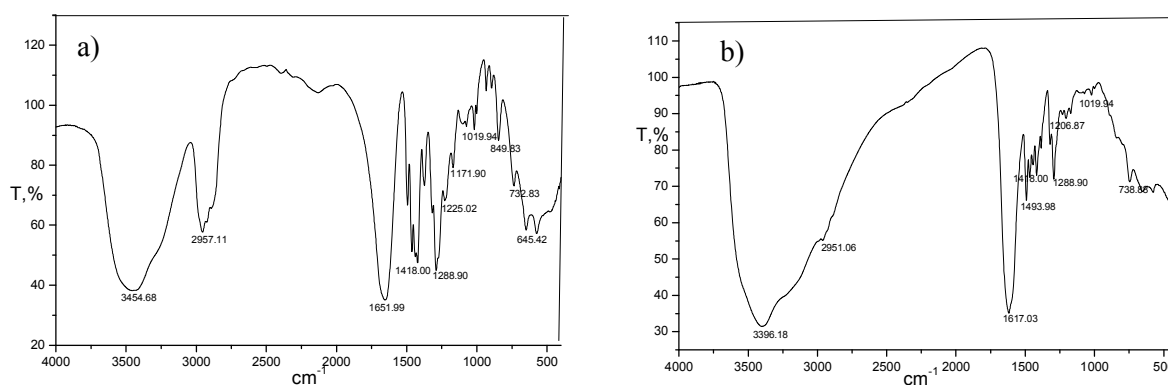
On the basis of thermodynamic constants of stability, using isotherm equations and isobars of Vant Hoff and Gibbs, changes of energy of Gibbs ($\Delta_r G^0$), an enthalpy ($\Delta_r H^0$) and an entropy ($\Delta_r S^0$) were calculated and presented in Table 3. As confirmation of a possibility of course of a complexing reaction in these systems in a forward direction serve the negative sizes of Gibbs' energy on the sign of the studied processes. Apparently from Table 3, interactions of iron ions with PVP are followed by exo-effects that point the negative values of change of an enthalpy during a reaction. Processes of formation of iron complexes with polyvinylpyrrolidone are characterized by the negative values of an entropy change. The negative values of change of an entropy ΔS at the negative change of an enthalpy ΔH says that the studied reaction is possible at rather low temperatures.

Table 3

Thermodynamic characteristics of complexing processes of PVP with Fe^{3+} ions

T, K	$lg\beta^0$	$-\Delta_r G^0, kJ/mol$	$-\Delta_r H^0, kJ/mol$	$-\Delta_r S^0, J/mol \times K$
298	31.00	176.849	725.653	1841.620
318	23.00	140.016	174.334	5041.910
333	10.10	64.397	1134.375	3213.150

The nature of the modifying effect of PVP on ions Fe (III) and a possible molecular structure of the PVP- $FeCl_3$ complex were studied by IR-spectroscopy (Fig. 5). The IR spectra of PVP and PVP- $FeCl_3$ complex are given in Figure 5. The characteristic peak of C=O bond in PVP becomes asymmetric after addition of the $FeCl_3$ complex that testifies to the strong coupling between PVP and Fe (III) in the PVP- $FeCl_3$ complex. IR spectra and PVP and the PVP- $FeCl_3$ complexes contain bands at 3454 and 3396 cm^{-1} characteristic for PVP. The carbonyl group in PVP is characterized by peak at 1652 cm^{-1} , widened because of double bond C=N in a lactam ring. This band is shifted to 1617 cm^{-1} in the PVP- $FeCl_3$ complex. Differences between the IR spectra of PVP and the PVP- $FeCl_3$ complex suggest strong donor-acceptor interaction between the oxygen atoms of the PVP ligand and the Fe (III) ions [25–27].

Figure 5. IR spectra of PVP (a) and complex $[Fe(PVP)_4(H_2O)_2]Cl_3$ (b)

The PVP ligand contains iminic bond C=N and demonstrates the polybasic behavior in aqueous solutions because of protonation/deprotonation of an oxygen atom, as shown in the Figure 6. The partially negative oxygen promotes interaction with the metals ions in solutions showing the strong ability to coordination with the transitional metals [28].

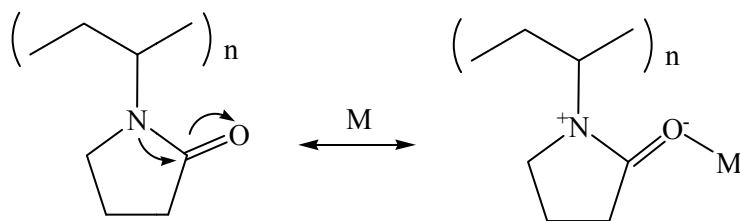


Figure 6. Resonance structure of lactam monomeric group of a polyvinylpyrrolidone, where M is an atom of metal

For a surface study of the polymer-metal complexes of iron a method of the scanning electron microscopy was used (Fig. 7). The analysis of images confirms formation of polymeric films with cellular non-uniform amorphous structure.

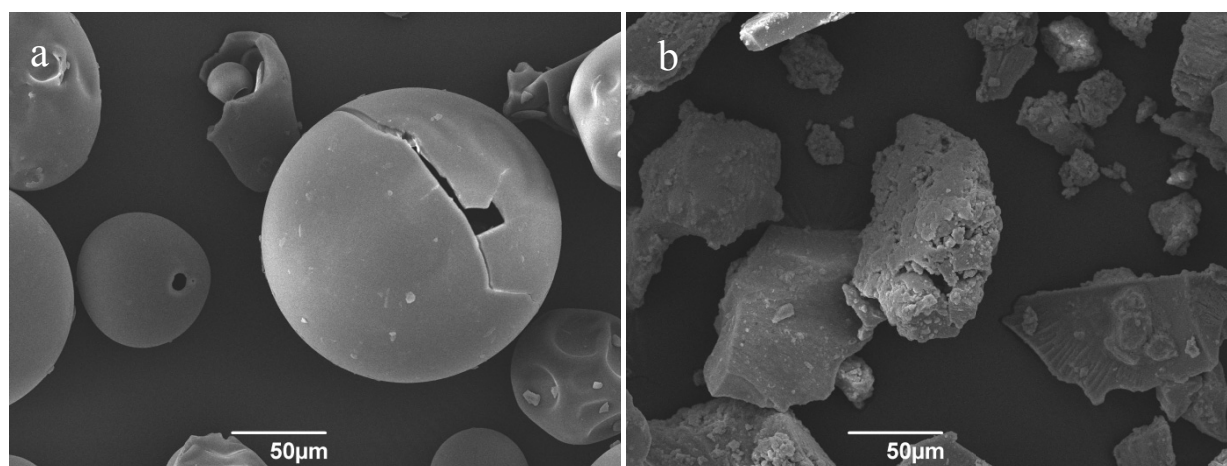


Figure 7. Images of PVP (a) and PVP-FeCl₃ (b) complex

Conclusions

An iron-polymer complex $[\text{Fe}(\text{PVP})_4(\text{H}_2\text{O})_2]\text{Cl}_3$ has been obtained from iron (III) chloride and polyvinylpyrrolidone (PVP). Using potentiometric and conductometric titration as well as IR spectroscopy, the structure of the polymeric complex was established and stability constants were calculated. Methods of an IR-spectroscopy and the scanning electron microscopy confirmed coordination of a polymeric ligand of PVP in a complex; the morphology and features of its surface were studied. It was established that atoms of oxygen of polymeric ligands shared in formation of a coordination bond with a metal ion. Results of an electron microscopy indicate amorphous structure of a complex.

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Темір (III) хлориді – поливинилпирролидон кешенді қосылысын синтездеу және құрамын зерттеу

Мақалада темір (III) хлориді және поливинилпирролидон негізіндегі полимерметалды кешенді қосылыс синтезделген. Оның құрамы потенциометрлік және кондуктометрлік әдістермен анықталған. Титрлеу қисықтары тұрғызылып, әрекеттесуші құраушылардың оңтайлы мольдік қатынастары табылған ($k = [\text{Fe}^{3+}]/[\text{ПВП}] = 0,24$). Алынған тәжірибелік мәліметтер темірдің полимерлі кешенді қосылысы түзілгендігін дәлелдейді, ондағы поливинилпирролидонның төрт монобуыны бір

кешентүзгіш металл–ионына сәйкес келеді. Металл–кешентүзгіштің координациялық қанығуы еріткіш молекулалары немесе темір тұзы анионы әсерінен болады. Ерітіндінің әртүрлі иондық күштерінде полимерлі кешенді қосылыстың тұрақтылық константалары Бьеррумның түрлендірілген әдісі бойынша есептеліп, сәйкесінше зерттеліп отырған үдерістің термодинамикалық тепе-теңдік константалары анықталған. Термодинамикалық тепе-теңдік константалары негізінде және Вант-Гоффтың изотерма-изобаралық теңдеулерін пайдалану арқылы Гиббс энергиясы ($\Delta_r G^0$), энтальпия ($\Delta_r H^0$) энтропия ($\Delta_r S^0$) мәндері есептелген. Реакция барысында энтальпия өзгерісінің мәні теріс болуы темір иондарының поливинилпирролидонмен кешентүзілу үдерісінің экзоэффект танытуынан деп түсіндірілді. Энтальпия өзгерісінің ΔH теріс мәнінде энтропия өзгерісінің ΔS теріс мәнге ие болуы зерттеліп отырған реакцияның төмен температураларда өту мүмкіндігі жоғары екендігін дәлелдейді. Полимерлі лиганд құрамындағы оттегі атомы кешентүзгіш металл-ионымен координациялық байланыс түзуге қатысатындығы анықталған. ИҚ-спектроскопия және сканирлеуші электронды микроскопия әдістерімен темір (III) хлориді – поливинилпирролидон негізіндегі синтезделген кешенді қосылыстың құрылысы мен морфологиясы зерттелген. Электронды микроскопия нәтижелері кешенді қосылыстың кеуекті біртекті емес аморфты құрылымды қабықша түзетіндігін көрсетті.

Кілт сөздер: поливинилпирролидон, темір, кешентүзілу, Бьеррум әдісі, константа, тұрақтылық, құрамы, термодинамика.

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Синтез и исследование состава комплекса хлорид железа (III) – поливинилпирролидон

В статье был синтезирован полимерметаллический комплекс на основе хлорида железа (III) и поливинилпирролидона. Потенциометрическим и кондуктометрическим методами был установлен его состав. Были построены кривые титрования и найдено оптимальное мольное соотношение реагирующих компонентов ($k = [\text{Fe}^{3+}]/[\text{ПВП}] = 0,24$). Полученные экспериментальные данные свидетельствуют об образовании полимерного комплекса железа, в котором на четыре составных монозвена поливинилпирролидона приходится один ион металла-комплексобразователя. Координационная насыщенность металла-комплексобразователя в этом комплексе осуществляется за счет молекул растворителя или аниона соли железа. На основании модифицированного метода Бьеррума были рассчитаны константы устойчивости полимерного комплекса при различных значениях ионной силы раствора, по которым были найдены термодинамические константы равновесия исследуемых процессов. На основании термодинамических констант устойчивости, используя уравнения изотермы и изобары Вант-Гоффа и Гиббса, были рассчитаны изменения энергии Гиббса ($\Delta_r G^0$), энтальпии ($\Delta_r H^0$) и энтропии ($\Delta_r S^0$). Реакции комплексообразования ионов железа с поливинилпирролидоном сопровождаются экзоэффектами, на что указывают отрицательные значения изменения энтальпии в ходе реакции. Отрицательные значения изменения энтропии ΔS при отрицательном изменении энтальпии ΔH говорят о том, что исследуемая реакция возможна при достаточно низких температурах. Установлено, что атомы кислорода полимерных лигандов принимают участие в образовании координационной связи с ионом металла-комплексобразователя. Методами ИК-спектроскопии и сканирующей электронной микроскопии исследованы строение и морфология синтезированного комплекса хлорид железа (III)-поливинилпирролидон. Результаты электронной микроскопии указывают на образование полимерных плёнок комплекса с пористой неоднородной аморфной структурой.

Ключевые слова: поливинилпирролидон, железо, комплексообразование, метод Бьеррума, константа, устойчивость, состав, термодинамика.

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