



Polymer-metal complex based on copper(II) acetate and polyvinyl alcohol: thermodynamic and catalytic properties

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Abstract

In this work we obtained a polymer-metal complex by mixing aqueous solution of copper(II) acetate with PVA at a certain ratio, pH of the solution and temperature. The composition of the complex compound was determined by potentiometric and conductometric titration. The possibility of a complex formation was proved by calculating thermodynamic characteristics. The stability constant of the polymer-metal complex was calculated on the basis of the modified Bjerrum's method. The metal-polymer complex was synthesized in the ratio 1:2. IR spectroscopy and scanning electron microscopy (SEM) confirmed the coordination of polymeric PVA ligand to copper and allowed evaluating the morphology and features of the complex surface. The catalytic activity of the synthesized compound was evaluated in the oxidation reaction of elemental phosphorus (P_4) by oxygen in aqueous-organic media under mild conditions. Quantitative analysis of phosphoric acid was made by photolorimetric method. We found that the oxidation process of P_4 in the presence of the complex $Cu(PVA)_2(OAc)_2$ in aqueous-organic media is characterized with the maximum absorption rate, in comparison with $Cu(OAc)_2 \cdot H_2O$ oxidation process with P_4 , and yields up to 97% of the products. The process of oxidation of yellow phosphorus by oxygen in the presence of the copper(II)-PVA complex proceeds through key reactions of two-electron reduction of the catalyst P_4 with the formation of intermediate phosphorus-containing products P^{3+} and the stages of catalyst regeneration by oxygen. Twenty-electron oxidation of P_4 to the phosphorus-containing P^{5+} products involves 10 two-electron redox reactions and a number of complexation or hydrolysis stages.

Keywords

copper(II) acetate
polyvinyl alcohol
polymer-metal complex
thermodynamic characteristics
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1. Introduction

The development of oxidation processes is essential in today's chemistry and industry [1–4]. Many oxidative techniques have been known to exist in natural life, and a lot of them have been used in various applications the industry, from wastewater treatment to cellulose or lignin bleaching [5–8]. Among these applications, oxidizing processes in the detergent industry, called bleaching, are particularly preferred for removing dyes [9–11].

In general, the stability and selectivity of homogeneous catalysts are strongly related to their molecular structure. Given the steric, electronic and conformational properties,

suitable ligands must be designed for metal complexes that function as effective catalysts. These ligands must also be flexible against oxidation and be electron donors in order to achieve high oxidation states of the active metal. Most of them are heat-sensitive substances and generally deteriorate above 150 °C [12–14].

Furthermore, the consideration of steric, electronic and conformational properties is necessary for the design of suitable ligands for metal complexes that will serve as effective catalysts.

Under heat treatment, polymers such as polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polystyrene (PS), etc., which have saturated main molecular chains and side

groups, can form conjugated structures by removing the side groups from the main one. Thermal degradation of polymers creates systems with delocalized π -electrons, which can lead to optical and electronic improvements. Then, polymer ligand synthesis and selective chelation of specific metal ions is an active research area [15]. Metal ions from polymer complexes have potential applications in electrolytes [16], sensors [17], stabilizers [18] and semiconductors [19]. Polyvinyl alcohol is an important material, given its large-scale applications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permeability, viscous media to control the crystallization process of salts, controlled monitoring of drugs or catalytic systems, etc. Polyvinyl alcohol (PVA) is a non-toxic, non-carcinogenic, biodegradable, biocompatible, water-soluble and inexpensive polymer. It could also be used for metal ions or salts in ecological composites [20]. PVA is a potential material that has a high dielectric strength, a good charge storage capacity and dopant-dependent electrical properties. It has a carbon-chain dorsal bone with hydroxyl groups attached to the methane carbons. OH groups can be a source of hydrogen bonds and can, therefore, help in the formation of polymer complexes. PVA has unique mechanical properties and exhibits both ionic and electronic conduction [21].

Despite certain achievements in the chemistry of elemental phosphorus (P_4), insufficient attention has been paid to the oxidative reactions involving P_4 in the catalytic regime, the description of their kinetics and mechanics, the identification of the nature of catalytically active intermediates.

Therefore, in this work, the optimal molar ratio of a complex compound based on copper(II) acetate and polyvinyl alcohol was studied. The possibility of a reaction of polymer-metal complex formation was studied by calculating thermodynamic characteristics. The complex was tested as catalyst in yellow phosphorus oxidation in aqueous-organic media under mild conditions.

2. Experimental

Copper(II) acetate $Cu(OAc)_2 \cdot H_2O$, polyvinyl alcohol (molecular mass 30 000, Sigma Aldrich), hydrochloric acid, sodium hydroxide, sodium chloride, toluene, distilled water were used without purification. Yellow phosphorus of the Shymkent Production Association "Phosphorus" (Kazakhstan) was used, which was previously mechanically cleaned from the oxide film under water. The concentration of P_4 in the obtained toluene solution (P_4 , mol/L) was determined by iodometric titration [22].

2.1. Synthesis of $Cu(CH_3COO)_2$ – PVA

A solution of 2.0 g (0.01 mol) of $Cu(OAc)_2 \cdot H_2O$ in 15 ml of distilled water was added to 15 ml of an aqueous solution of 0.88 g of PVA (0.02 mol). The resulting mixture was stirred by magnetic stirrer for 1 hour at ambient temperature until the polymer was completely dissolved and bound to Cu(II)

ions. The synthesized light-green complex was dried and stored in air at room temperature. Yield: 3.15 g (98%).

The process of complex formation between copper(II) ion and PVA was investigated by potentiometric and conductometric methods with several ionic strengths and temperatures. Potentiometric studies were carried out in thermostated conditions on an ionomer pX-150MI using silver chloride and glass electrodes. The accuracy of the pH measurement was 0.02 pH units. Conductometric studies were performed on a ConductivityMeter 13701/93 device (PHYWE) under thermostatically controlled conditions. The polymer-metal complex was obtained by mixing aqueous solution of copper(II) acetate with PVA at certain ratio, pH of the solution and temperature. The stability constant of the polymer-metal complex was calculated on the basis of the modified Bjerrum's method.

IR spectra of PVP and Cu(II)-PVA complex were recorded on a FT IR-4100 type A JASCO instrument in the range of 4000–450 cm^{-1} . 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).

Quantitative analysis of phosphoric acid was performed by photolorimetric method on a spectrophotometer SPEKOL 1300 (ANALYTIK JENA, Germany).

2.2. Typical Reaction Procedure

Oxidation of yellow phosphorus by oxygen was carried out on a temperature-controlled laboratory setup with intensively stirred up glass temperature-controlled reactor with negligible temperature gradient "a catalytic duck", supplied by the potentiometric device and connected to the gas burette filled with oxygen. The laboratory experiments were made as follows. The reactor with a total volume of 150 mL was charged with the catalyst (1.07 mmol) under an oxygen atmosphere. The reactor and the gas burette were preheated to 60 °C. The temperature was maintained by the water circulating between the glass reactor and the heating devices. Then, in oxygen flow, a solution of P_4 in toluene (1.07 mmol) was added to water (9 mL, 9:1 by volume), and an electric motor was switched on. During the catalytic reaction the rates of oxygen absorption were recorded in certain intervals. The temperature was maintained with an accuracy of ± 0.5 °C by means of the thermostat. After the experimental runs, the reaction solutions were mixed together and analyzed on a spectrophotometer.

3. Results and discussion

3.1. Potentiometric titration

Figure 1 shows the potentiometric titration curve of $Cu(OAc)_2$ – PVA complex. The mixing of solutions of polymer with salt is accompanied by a pH decrease, which is explained by the deprotonation of initially protonated PVA during the complexation.

From the titration curve (Figure 1), the optimal molar ratio of the reacting components k ($k=[Cu^{2+}]/[PVA]=0.50$) was found. It means that one central metal atom bonds with two mono-links of polymer ligands.

3.2. Conductometric titration

In order to confirm the composition of the formed PVA-Cu²⁺ complex, the dependence of the conductivity corrected for the viscosity on the ratio of the initial component of the system was studied (Figure 2).

The increase in electrical conductivity is due to the released H⁺ ions during the reaction between PVA and copper(II) ions. As can be seen from Figure 2, the electrical conductivity of the solution with an increase in the molar content of metal ions passes through the inflection point. Based on the data obtained as a result of conducted conductometric studies, it can be argued that the complexation process is accompanied by an increase in the electrical conductivity of the system at the ratios PVA-Cu²⁺=2:1.

In the process of complexation of the PVA polymer ligand, their hydrodynamic dimensions decrease (chelate effect); protons are released, as evidenced by the experimental results. Thus, it can be assumed that the complex of the composition is formed in the PVA-Cu²⁺ system.

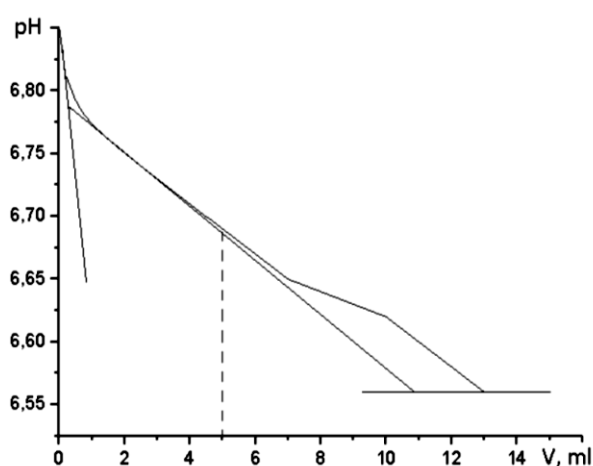


Figure 1 Curve of potentiometric titration of PVA (10^{-2} M) with copper salt $Cu(OAc)_2$ (10^{-2} M) (where V - titrant volume in mL, pH - pH of solution).

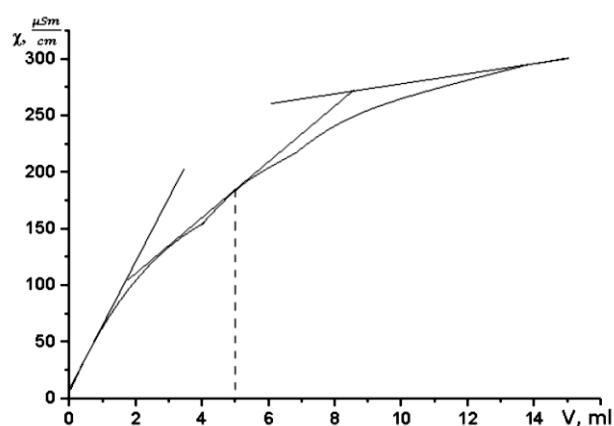


Figure 2 Curve of conductometric titration of PVA (10^{-2} M) with copper salt $Cu(OAc)_2$ (10^{-2} M) (where V - titrant volume in ml, χ - specific electrical conductivity of solution in $\mu S/cm$).

3.3. Modified Bjerrum's method calculations

The stability constant of the resulting polymer complex and the coordination number of copper(II) were calculated using the modified Bjerrum's method. In accordance with the known method, the potentiometric study was carried out at three values of the ionic strength of the solution: 0.01, 0.05, and 0.1 mol/L, and the polymer ligand solution was titrated with hydrochloric acid (HCl), depending on the nature of the complexing metal salt, with a change in the pH of the medium in the absence and presence of metal ion, as well as at several temperatures (25, 45, 70 °C). Figure 3 shows the pH value change in the absence and presence of metal ions during the experiment. It is clearly seen that the pH value in the presence of metal ions is higher than in experiment without metal ions. It signifies the formation of the complex and means that the system reacts in the acidic medium.

Table 1 shows the values of the Bjerrum's formation functions (n) corresponding to the coordination number of the metal complexing agent at three ionic strengths and at 70 °C. The data obtained indicate the formation of a copper polymer complex in which the coordination number of the metal is equal to two.

3.4. Thermodynamic parameters of the process

The knowledge of the thermodynamic parameters (changes in Gibbs' energy ($\Delta_r G^0$), enthalpy ($\Delta_r H^0$) and entropy ($\Delta_r S^0$)) of the studied process is necessary for the scientifically based choice of the optimal conditions for its implementation in practice. Moreover, many researchers admit that the fundamental laws of thermodynamics, which were established for the systems consisting of low molecular weight compounds, can be applied to the systems involving macromolecules [23].

The PVA-Cu(OAc)₂ system is characterized with the negative Gibbs' energy, which indicates the spontaneous occurrence of the studied process in the direction of the compound formation (Table 2).

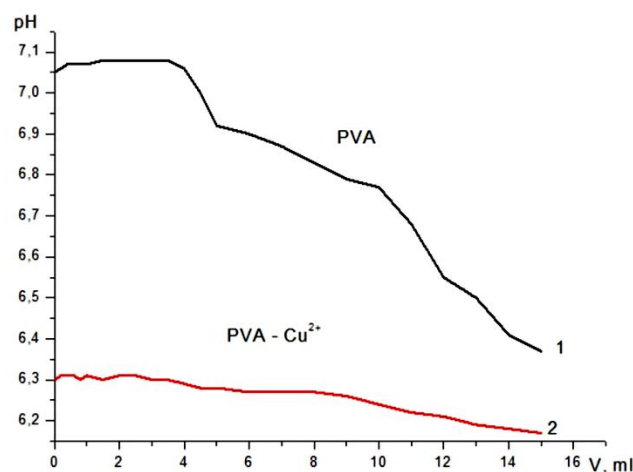


Figure 3 Curves of potentiometric titration of aqueous solutions of polyelectrolyte of PVA (10^{-2} M) (1) and PVA - Cu^{2+} (10^{-2} M) (2) by hydrochloric acid (10^{-2} M) and $L_f=0.01$, $T = 25$ °C.

In the temperature range of 25–70 °C, the complexation process of PVA with Cu²⁺ ion is accompanied by the release of heat (exothermic process), as a result of which the strength and stability of the polymer-metal complex decreases with temperature increasing.

Thus, based on analysis of the results of potentiometric and conductometric analysis, the formation of copper(II)-PVA polymer complex and its composition were established.

3.5. IR spectroscopy and SEM studies

The process of the formation of the copper(II)-PVA complex is characterized by the negative value of the change in entropy, which is caused by the existence of donor-acceptor bond in the studied complex. This also indicates that the ratio between copper(II) ion and PVA is 1:2. To study the surface of the pure polymer and the polymer-metal complex, the scanning electron microscopy (SEM) method was used; the results of the study are presented in Figures 4 and 5. A comparison of microscopic images of the pure polymer and the resulting complex indicates the formation of porous spherulites of different sizes.

The infrared spectrum was acquired for polyvinyl alcohol and the complex copper(II) acetate – PVA (Figure 6).

Table 1 Values of Bjerrum’s formation functions of the Cu(OAc)₂ – PVA complex at 70 °C and I = 0.01 mol/L.

[LH ⁺] $\cdot 10^4$ (mol L ⁻¹) ^a	pL ^b	L $\cdot 10^6$ (mol L ⁻¹) ^c	L _c $\cdot 10^3$ (mol L ⁻¹) ^d	n ^e
3.33	5.39	4.12	3.00	2.00
6.66	6.04	0.922	2.67	1.78
9.99	6.33	0.462	2.33	1.56
13.30	6.69	0.206	2.00	1.33
16.60	6.83	0.149	1.67	1.11
20.00	7.22	0.0597	1.34	0.89
23.30	9.42	0.000381	1.00	0.67
26.60	10.67	0.0000213	0.67	0.45
30.00	12.29	0.000000517	0.34	0.23
33.3	13.91	0.0000000124	0.014	0.01

^a [LH⁺] – concentration of the protonated ligand groups;

^b pL or -lg[L] – concentration of the free ligands calculated on Henserson-Hasselbach equation pH = pK_α + mlg[L]/[LH⁺], where m – the empirical coefficient considering interlink interaction of a polymeric chain;

^c [L] – concentration of the free ligands which are not involved in a complexing process;

^d [L]_c – concentration of the ligand groups connected in a complex;

^e n – Bjerrum’s formation functions or average coordination number of a metal ion.

Table 2 Thermodynamic characteristics of the complexation.

T, °C	-Δ _r G ^o , kJ/mmol ^a	-Δ _r H ^o , kJ/mmol ^b	-Δ _r S ^o , kJ/mmol·K ^c
25	0.32	1.6328	0.004405
45	0.23	1.0900	0.002704
70	0.16	1.3502	0.003470

^a Δ_rG^o – Gibbs’s energy change of reaction;

^b Δ_rH^o – enthalpy change of reaction (heat effect);

^c Δ_rS^o – entropy change of reaction.

By comparing these two IR spectra, a displacement of the band position ν_{O-H} is clearly seen. In the polyvinyl alcohol infrared spectrum, the position of ν_{O-H} changes from 2390 to 2410 upon complexation with Cu(II), which can be seen in the infrared spectrum of the complex based on copper(II) acetate – polyvinyl alcohol, indicating its participation in the formation of copper – polymer complex [20]. It gives strong indication of specific interactions between the ligand and metal ion.

3.6. Oxidation of yellow phosphorus (P₄) catalyzed by Cu(PVA)₂(OAc)₂ complex under mild conditions

The synthesized catalyst was used in the process of oxidation of phosphorus at room temperature in the presence of oxygen at atmospheric pressure:

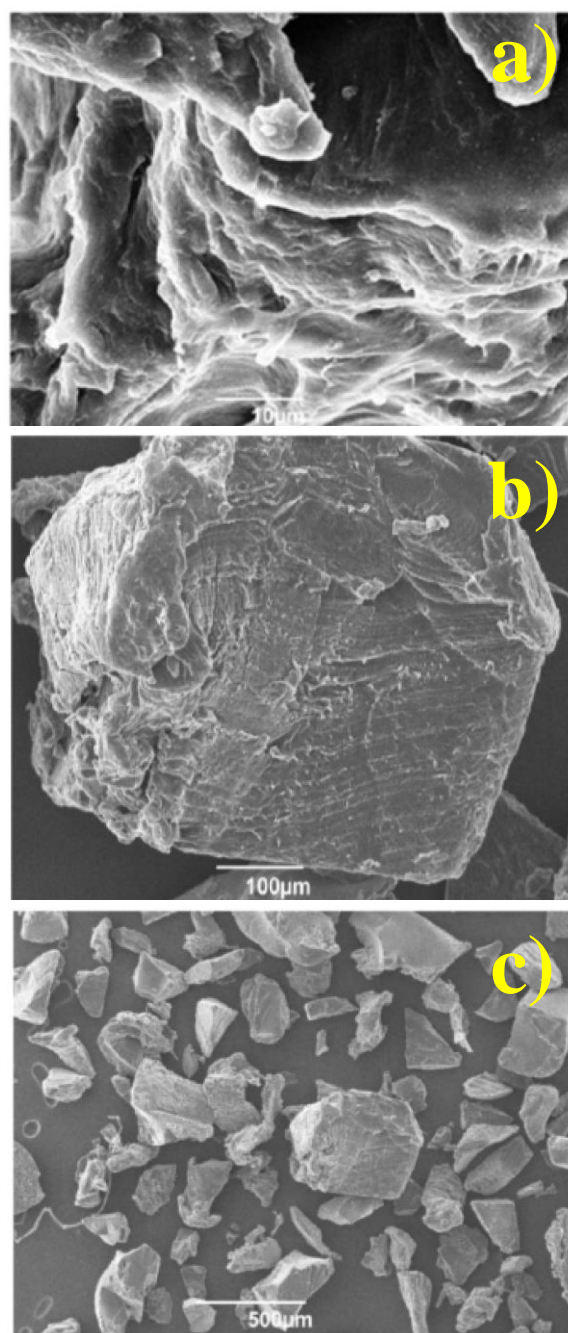


Figure 4 SEM micrographs of polyvinyl alcohol.

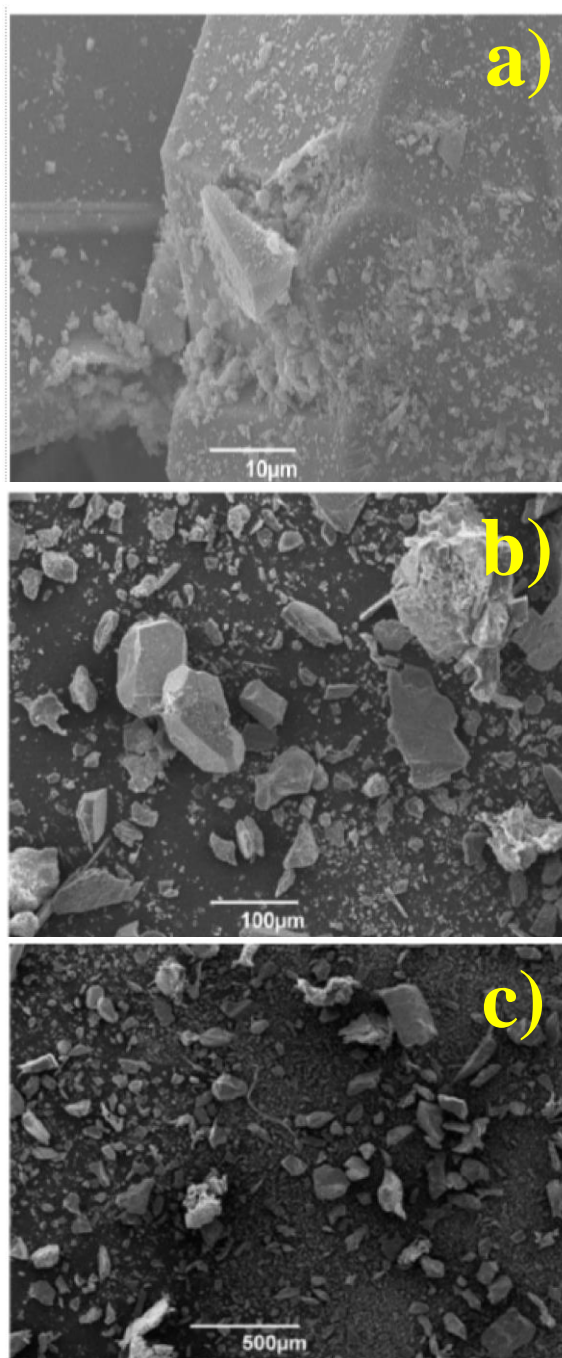


Figure 5 SEM micrographs of copper(II) acetate-PVA complex.

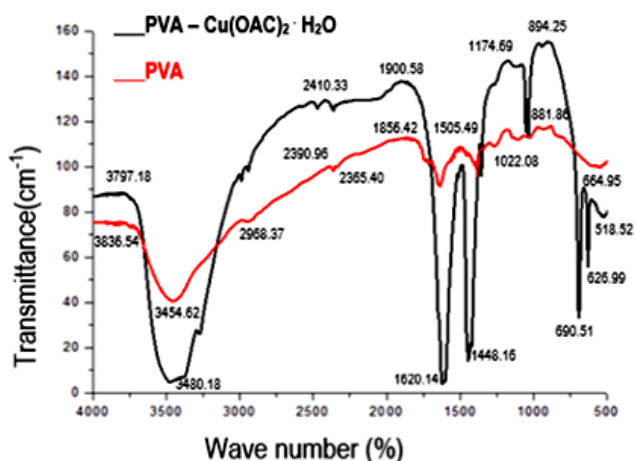
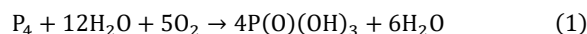


Figure 6 IR – spectra of PVA and PVA – Cu(OAc)₂·H₂O.



The results of the oxidation reaction studies at 60 °C were presented in the mole ratio of the reagents [Cu(PVA)₂(OAc)₂]:[P₄] = 1:1; 3:1; 6:1.

During the interaction of yellow phosphorus with aqueous alkali solutions at 50°C due to poor solubility of phosphorus ($S_{500\text{ }^\circ\text{C}} = \sim 3 \cdot 10^{-3}$ g/L) a slow disproportionation reaction takes place with the formation of hypophosphite and PH₃ [24].

Figure 7 shows the typical kinetic curves of P₄ oxidation process in the solution of Cu(PVA)₂(OAc)₂-C₇H₈-H₂O. The reaction proceeds in an unsteady mode. Both the kinetic (W-τ) and the conversion (W-Q) curves go through maximum as in the case of non-modified Cu(OAc)₂. The average duration of experiments was 130 minutes. The maximum oxygen absorption rate was observed for the molar ratio of [Cu(OAc)₂]:[P₄] and [Cu(PVA)₂(OAc)₂]:[P₄] of 6:1.

The experiment of the oxidation process with P₄ in the presence of the complex Cu(PVA)₂(OAc)₂ was characterized with the maximum absorption rate, in comparison with Cu(OAc)₂·H₂O.

The reaction conditions and product yield of P₄ oxidation by O₂ with Cu(OAc)₂·H₂O and Cu(PVA)₂(OAc)₂ in aqueous-organic solutions are presented in Table 3.

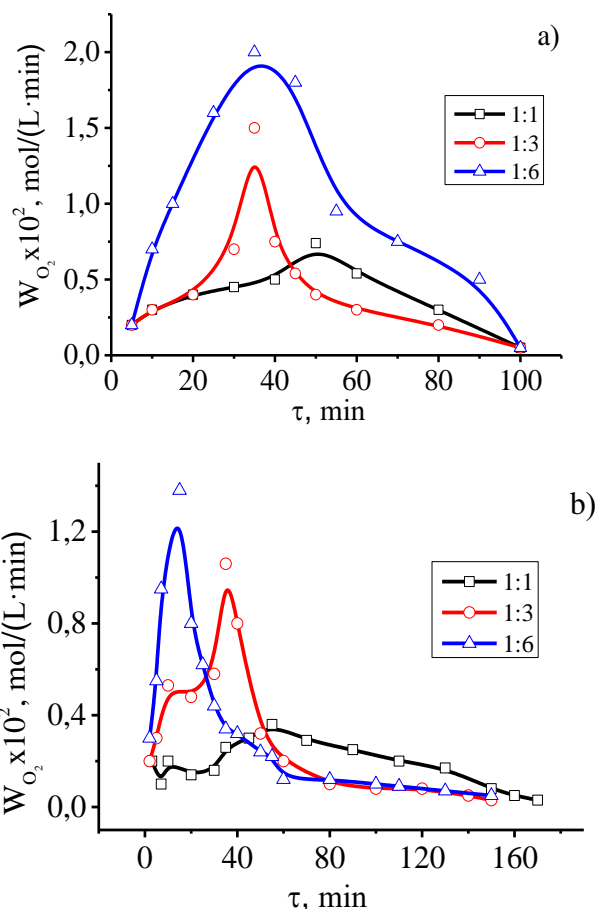


Figure 7 The kinetic curves (W-τ) of the oxidation process of P₄ with oxygen in aqueous-organic medium in the presence of Cu(OAc)₂·H₂O (a) and Cu(PVA)₂(OAc)₂ (b) complex. Reaction conditions, mol/L: [P₄] 1.07; [H₂O] 50; [C₇H₈] 0.94; 60 °C; [Cat]: 1 - 0.01; 2 - 0.03; 3 - 0.06.

Table 3 Oxidative hydrolysis of yellow phosphorus with copper(II) acetate and copper(II) acetate – PVA at 60 °C.

Runs	Composition of solution, mol/L				T, °C	Time, min	Yield of products, %	
	Cat	P ₄	H ₂ O	C ₇ H ₈			I	II
Cat Cu(OAc) ₂ ·H ₂ O								
1	1.07	1.07	50	0.94	60	120	21	40
2	3.21	1.07	50	0.94	60	120	27	47
3	6.42	1.07	50	0.94	60	120	33	55
Cat Cu(PVA) ₂ (OAc) ₂								
1	1.07	1.07	50	0.94	60	120	27	47
2	3.21	1.07	50	0.94	60	120	37	53
3	6.42	1.07	50	0.94	60	120	40	57

Note: I – (HO)₂HPO; II – (HO)₃PO.

The P₄ molecule, its inorganic and organic derivatives are prone to two-electron oxidation in aqueous solutions: P₄→4P⁺; P⁺→P³⁺; P³⁺→P⁵⁺. It is known that the products of two-electron oxidation of P₄ are stable compounds P₄(OR)₂, P₄(OR)₄, P₂(OR)₄, P(OR)₃, P(OR)₅, while the products of one-electron oxidation of P₄ are unstable radicals [25]. They are strong two-electron reducing agents and impose the role of a two-electron oxidizer on Cu(II) complexes [26]. The standard reduction potentials of Cu(II) indicate that, depending on the redox partner, Cu(II) can be reduced to Cu(I) or Cu. The Cu(II) ion is prone to both single-electron ($E_{Cu(II)/Cu(I)} = 0,538\text{ V}$) and two-electron reduction ($E_{Cu(II)/Cu(0)} = 0,337\text{ V}$).

4. Conclusions

In this study, the ratio of components in a complex compound based on copper(II) acetate and polyvinyl alcohol was determined by the potentiometric method. Two monolinks of polymers connect to one complex – forming metal ion. In addition, the results of the conducted conductometric work also proved that the metal-ligand ratio is 1:2. Microphotographs taken with SEM showed the formation of porous spherulites of various sizes. As a result of IR spectroscopy, it was shown that the peak corresponding to the ν_{O-H} subgroup in the polymer-ligand shifted in a complex compound from 2390 to 2410 cm⁻¹.

The thermodynamic characteristics of the complex compound based on copper(II) acetate and polyvinyl alcohol were calculated, and it was found that the Gibbs' energy value is a negative. The process of complex formation occurs spontaneously. The value of the enthalpy is also negative, and with an increase in temperature, it is assumed that the reaction will shift in the opposite direction.

The maximum oxygen absorption rate was observed in the case of the molar ratio [Cu(PVA)₂(OAc)₂]:[P₄] = 6:1 with yield of final products up to 97%.

Supplementary materials

No supplementary materials are available.

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Author contributions

Conceptualization: D.N.A., B.S.B.

Data curation: D.T.K., A.T.O.

Investigation: K.S.M., D.T.K., A.T.O.

Project administration: D.N.A.

Writing – original draft: D.T.K., B.S.B.

Writing – review & editing: K.S.M., D.N.A.

Conflict of interest

The authors declare no conflict of interest.

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