

groups, can form conjugated structures by removing the side groups from the main one. Thermal degradation of polymers creates systems with delocalized  $\pi$ -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  $\pm 0.5$  °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.