

Review

Metal–polymer complex catalysts on the base of polyethyleneimine for oxidation of sulfides

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Abstract

A number of metal–polymer complex catalysts on the base of cross-linked polyethyleneimine with copper or nickel ions were prepared using the principle of prearrangement of polymer to complexing metal ions. The investigation demonstrated a high activity of prearranged complexes of copper(II) in the oxidation of sulfide by oxygen under mild conditions compared to complexes with nickel(II) and cobalt(II). It has been shown that the activity of heterogeneous copper(II) containing polymer catalysts prearranged for copper(II) is comparable to the commercially employed water soluble cobalt(II) phthalocyanine tetrasulfonic acid.

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1. Introduction

Complexes of transition metals with complex-forming polymers are efficient catalysts of various chemical processes [1,2]. Use of such polymers as solid support opens new possibilities of varying ligand surrounding and control of catalytic properties

of the complexes. The principle of prearrangement of complex-forming polymers to complexing metals developed earlier [3–5] is based on the use of the memory of the polymer composition and consists in the interaction of non-cross-linked polymers with complexing metal ions in rather dilute solution followed by fixation of the conformations optimum for complex formation by intermolecular cross-linking and removal of metal ions from the cross-linked system. It was shown that cross-linked macromolecules may “keep in mind” conformations favourable for complex formation with metal ions they had been prearranged for. This results in substantial improvement of complexing char-

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acteristics of polymers, which allows to prepare catalysts with improved catalytic properties on their base. By ESR analysis it was demonstrated that due to prearrangement more homogeneous and more uniformly distributed complexes were formed. The structure of prearranged complexes is comparable to that of complexes formed by their low-molecular analogues in solution [5]. It is known that the homogeneous active centre is necessary prerequisite for the preparation of highly active and selective catalysts.

In case of low concentrations of toxic sulfide in the waste water from petrochemical processes detoxification can be carried out by bacteriological oxidation. However, at concentrations above 70 mg/l sulfide bacteriological metabolism is suppressed. But waste water from petrochemical processes sometimes contains sulfide up to 25 000 mg/l. In this case sulfides can be removed using strong oxidizing agents (H_2O_2 , NaOCl) or, preferably, using catalysts for catalytic oxidation at mild conditions. Water soluble cobalt phthalocyanine complexes, such as cobalt(II) phthalocyanine tetrasulfonic acid (CoPTS), are used as catalysts for oxidation of sulfides by oxygen [1,2,6–16]. We have shown that prearranged complexes of copper(II) with amine containing polymers are efficient catalysts in the oxidation of hydrocarbons [4,14].

In this paper we describe the use of prearranged cross-linked complexes of transition metal ions with poly(ethyleneimine) (PEI) as catalysts for the oxidation of sulfides at mild conditions. It is known that PEI forms complexes with copper, nickel and cobalt ions (Pomogailo in Ref. [2]).

2. Experimental

2.1. Reagents and apparatus

The sodium sulfide content of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Aldrich) was determined as described in Ref. [16]. Copper sulfate pentahydrate, nickel chloride hexahydrate, cobalt hexahydrate chloride and *N,N'*-methylenebisacrylamide were purchased from Aldrich and used as received. PEI in a form of 50% water solution with molecular mass 50 000–60 000 from Acros was used. CoPTS was prepared as described [17].

All experiments for the catalytic oxidation of sulfide were carried out at 293 ± 0.1 K in a 100-ml glass reactor with a temperature controlled jacket and magnetic stirrer connected by a glass tube with a 50 ml gas burette as described in Refs. [15,16]. Standard borate buffer solution (50 ml) of pH 10 and a catalyst—from 2.5 to 20 mg (from 0.005 to 0.04 mmol metal salt) was placed into reactor. The system was being purged with oxygen for 10 m, and 1 ml of an aqueous solution containing 2 mmol of sulfide was added. The molar ratio Na_2S : metal varied in the range of 50:1–400:1. In some cases the reaction vessel was irradiated with visible light using a halogen lamp (light intensity 180 mW/cm^2) [16,17].

Cyclic voltammetry of the polymer metal complexes was carried out using an Autolab PGSTAT12 potentiostat (Eco Chemie, Utrecht, The Netherlands) in a three-electrode configuration with an Ag/AgCl/KCl (3 M) reference electrode, a platinum-wire counter electrode and a platinum-disk (1 mm)

working electrode (speed of scanning was 5 mV/s). Experiments were carried out in a 50 ml cell, into which 20 ml of buffer solution containing 300 mg of PEI and 0.6 mmol of a metal salt was poured. About 20 μl of 1 M solution of sulfide containing 0.02 mmol of Na_2S was added to the solution of complexes.

2.2. Synthesis of prearranged metal–complex catalysts

For preparation of prearranged catalysts 7 ml of 0.5 M solutions of copper or nickel nitrates (3.5 mmol of metal) were added to 10 ml of 10% aqueous solution of PEI. *N,N'*-methylenebisacrylamide as a cross-linking agent in the amount of 20% PEI was added to the solutions of the formed complexes. Then, water was removed by evaporation in vacuum and the complexes with dispersed cross-linking agent were heated at 130°C for 7 h in vacuum at 10^{-3} to 10^{-4} Torr. Metal ions were removed from the cross-linked complexes with 1 M solution of hydrochloric acid. For comparison, non-prearranged catalysts were also obtained using the same procedure but without metal ions. Metal ions were introduced into cross-linked polymers by contacting them with 0.05 M solution of a copper, nickel or cobalt salt. The complexes were treated with 1 M HCl and the amount of copper(II) in desorbate was determined by titration with disodium salt of ethylenediaminetetraacetic acid, whereas amount of cobalt(II) and nickel(II) was determined by photometry.

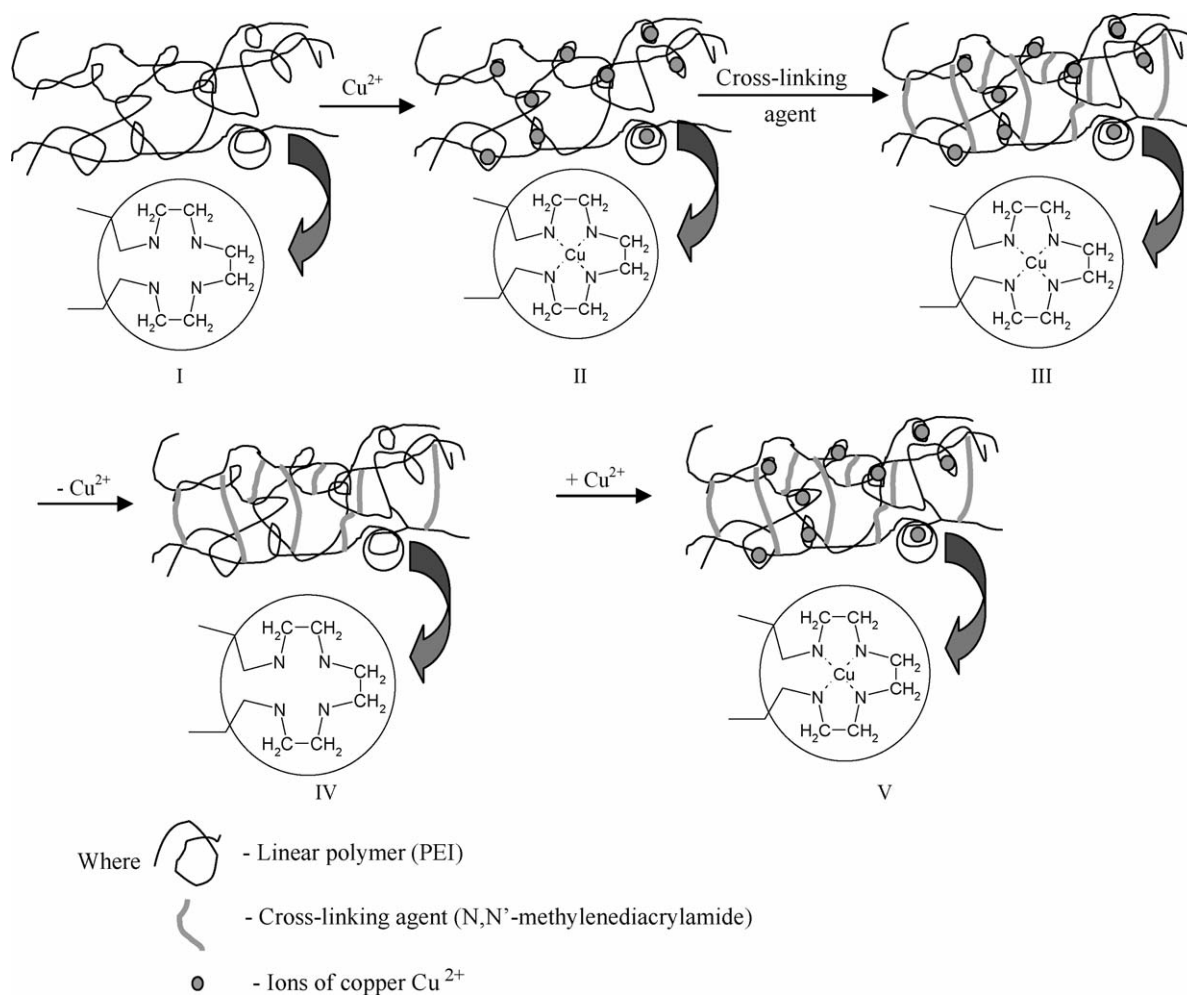
3. Results and discussion

3.1. Prearrangement of metal–complex catalysts

The preparation of prearranged metal–complex catalysts was carried out as follows (Scheme 1). In the first step non-cross-linked PEI (I) interacts with copper ions forming the non-cross-linked complex (II). Then, in the second step the conformation of the PEI favourable for complexation with copper(II) is fixed by cross-linking (III). Finally, in the third step copper ions are removed from the cross-linked system by treating it with 1 M hydrochloric acid. Product III is a metal–polymer complex. When studying complexes of copper with polymers ESR spectroscopy demonstrated significant changes in the structure of the prearranged complexes compared to non-prearranged ones. Introduction of paramagnetic ions (Cu^{2+}) as a label allows carrying out ESR study of the complexes prearranged for nickel. Selection of synthesis conditions and ions loading makes it possible to regulate the ratio between individual complexes and magnetic associates in the polymer phase. The characteristics of the formed complexes are given in Ref. [5].

Conformational prearrangement of PEI based polymers promotes, on subsequent bonding with metal, preferential formation of uniform complexes with the structure identical to their low-molecular analogs in solution. Whereas in case of non-prearranged complexes various structures are formed (see Scheme 2).

In prearranged complexes copper is also more uniformly distributed within the specimen volume comparing to non-



Scheme 1. Scheme of the synthesis of the polymer metal complexes on the base of PEI prearranged for copper(II).

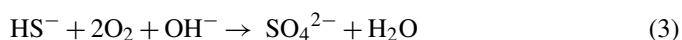
prearranged ones. It is especially important when using complexes of transition metals with polymers as catalysts. This is a prerequisite for the formation of uniform active centers, which is an important condition for preparation of selective catalysts.

Repeated sorption of the metal ions by the prearranged polymer allows formation of uniformly distributed metal ions in a polymer phase with a structure similar to that of complexes formed by non-cross-linked polymers in solution [5]. For comparison the preparation of non-prearranged metal–complex catalysts is shown in Scheme 2.

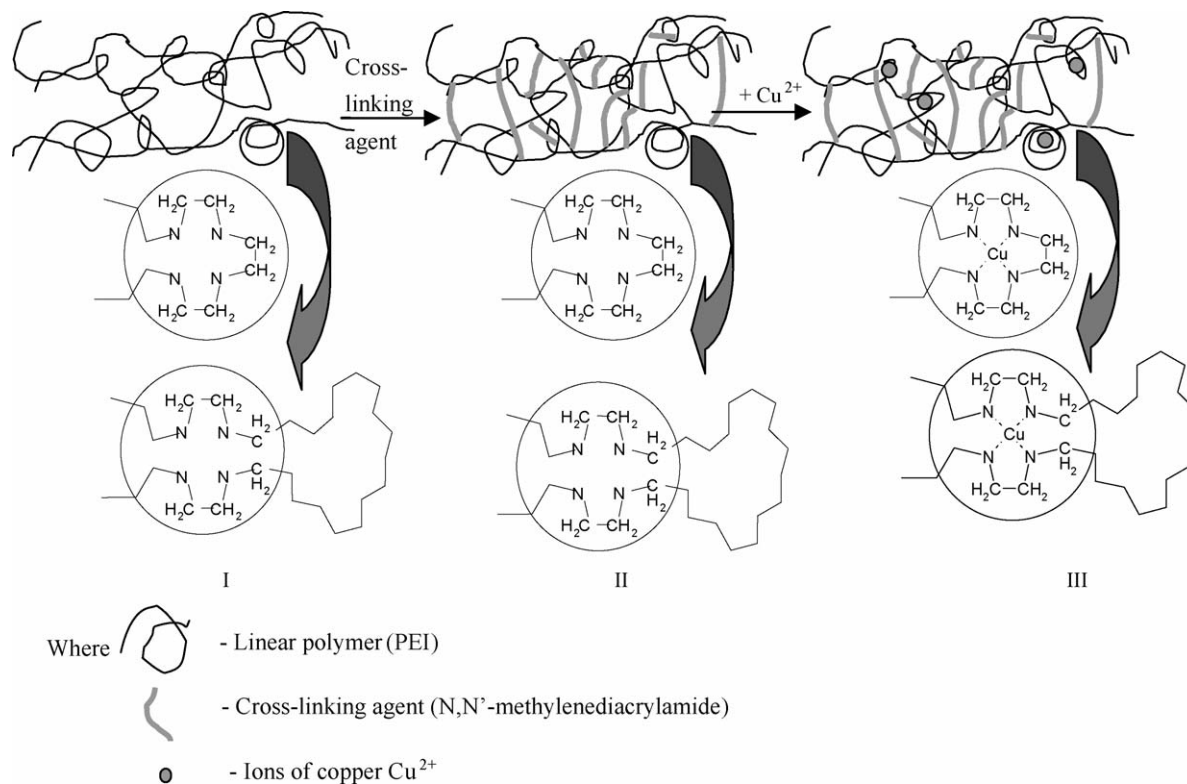
3.2. Catalytic oxidation of sulfides

The catalytic oxidation of sulfides can lead to different reaction products [15], such as sulfur (Eq. (1), 1 mmol employed sulfide consumes 12.3 ml oxygen), thiosulfate (Eq. (2), 1 mmol employed sulfide consumes 24.5 ml oxygen) and sulfate (Eq. (3), 1 mmol employed sulfide consumes 49.0 ml oxygen). The results of the catalytic oxidations show that after 3600 s reaction time up to ~50 ml oxygen was consumed for the formation of sulfate. Intermediate oxygen consumption corresponds to intermediate

oxidation products [15]. The mechanism of the catalytic oxidation of sulfide discussed in literature is quite complicated due to several possible intermediates and their formation depends on the kind of catalyst and the reaction conditions [6,15]. In principle, first coordination of sulfide anion and oxygen occurs at free axial positions of the quadratic planar metal complex (Scheme 3). Then, electron transfer under oxidation of sulfide and reduction of oxygen takes place and formed hydrogen peroxide is involved in the oxidation process:



In Table 1 the catalytic activity of the prepared polymer metal complexes in the oxidation of sulfide is compared with the well known and highly active CoPTS. It can be seen that irradiation does not significantly influence the oxygen consumption. This means that no light induced reactions are involved in the oxidation of sulfide. In contrast, zinc(II) complexes of phthalocyanines are photocatalytically active [6].



Scheme 2. Scheme of the synthesis of the polymer metal complexes on the base of PEI non-prearranged for copper(II).

It can be seen from Table 1 that decrease of the amount of metal reduces catalytic activity of the copper complexes. Complexes of cobalt and nickel with equal content of the metal exhibit lower catalytic activity compared to copper complexes. It might be explained by the more complicated tetrahedral structure of cobalt and nickel complexes compared to planar copper complexes.

Heterogeneous prearranged polymer copper catalysts on the base of PEI exhibit a catalytic activity which is comparable to the activity of dissolved cobalt(II) phthalocyanine tetrasulfonic acid. The high catalytic activity of amino groups containing polymer

copper complexes in oxidation reaction is apparently related to the structure of copper complexes formed in a catalyst phase (Fig. 1). Earlier we have shown that prearrangement of polymers for copper ions provides a substantially uniform distribution of the copper ions and that copper is coordinated with four amino groups [5].

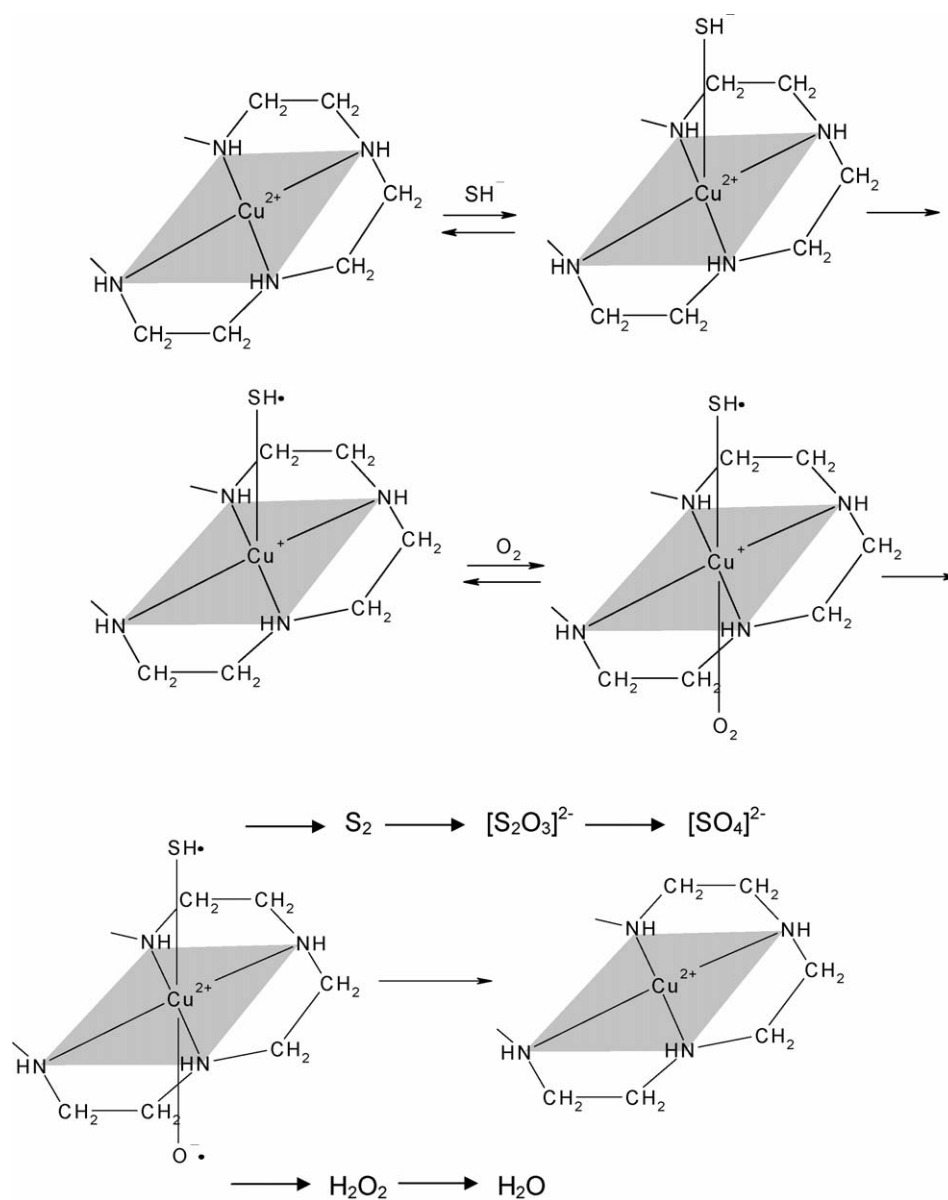
Nickel(II) complexes usually do not exhibit high catalytic activity in oxidation reactions. Cobalt(II) complexes in amino groups containing polymers are coordinated with six amino groups (Pomogailo in Ref. [2]). Therefore, adsorption of a substrate onto cobalt ions is sterically hindered. Presumably in the

Table 1
Oxidation of sodium sulfide by polymer metal complexes and CoPTS

Sample	Ratio $\text{Na}_2\text{S}:\text{metal}$	Type of reaction ^a	Initial rate (ml O_2/min)	Induction period (s)	Volume of oxygen consumed during 3600 s (ml)	Volume of oxygen consumed during 3600 s (mmol)
Non-prearranged PEI with Cu	50:1	C	0.70	40	32.6	1.33
Non-prearranged PEI with Cu	50:1	PC	0.75	35	34.8	1.42
Prearranged for copper PEI with Cu	50:1	C	3.75	25	45.0	1.84
Prearranged for copper PEI with Cu	100:1	C	1.20	30	38.1	1.56
Prearranged for copper PEI with Cu	200:1	C	0.85	50	31.6	1.29
Prearranged for copper PEI with Cu	400:1	C	0.67	100	27.6	1.13
Prearranged for nickel PEI with Ni	50:1	C	0.30	5	15.7	0.64
Prearranged for copper PEI with Co	50:1	C	0.42	80	15.4	0.63
CoPTS ^b	50:1	C	3.95	0	50	2.04
CoPTS ^b	50:1	PC	2.70	0	50	2.04

^a C, catalysis without irradiation; PC, photocatalysis under irradiation.

^b CoPTS, cobalt(II) phthalocyanine tetrasulfonic acid.



Scheme 3. Scheme of catalytic oxidation of sulfide by the polymer copper(II) complexes on the base of PEI.

presence of amino groups and oxygen, oxidation of bivalent cobalt to trivalent one takes place and the latter one forms stable complexes with amino groups. Hence, adsorption of sulfide ions onto active centers of the catalyst is even more hindered. Apparently this is the reason of the low activity of cobalt(II) containing catalytic centers in PEI.

In order to confirm the redox activity of metal ions in polymer metal complexes as shown in Scheme 3, cyclic voltammograms of the non-cross-linked PEI complexes in aqueous solution were measured in the potential range of -0.2 to $+0.6$ V against Ag/AgCl under air. In the absence of sodium sulfide the polymer copper complex shows the reduction of Cu^{2+} to Cu^+ whereas in the case of the polymer nickel and cobalt complexes no redox behaviour is seen (Fig. 2). After addition of an excess Na_2S to the copper complex solution no reduction wave is observed (Fig. 3).

Probably this may be due to the formation of Cu^+ by the excess of Na_2S . The polymer nickel complex exhibits no change when compared with the voltammogram in the absence of sulfide. In contrast, the polymer cobalt complexes demonstrate irreversible oxidation of cobalt from the bivalent to the trivalent oxidation state at ~ 300 mV. It can be explained as follows. It is known that ammonia salts of bivalent cobalt are easily oxidized into the corresponding salt of trivalent cobalt in the presence of atmospheric oxygen. At the same time cobalt(II) sulfide may precipitate without atmospheric oxygen in a form of bivalent cobalt, however in a presence of air it is spontaneously transformed into trivalent cobalt. The oxidation peak at ~ 300 mV (Fig. 3) observed on addition of sodium sulfide to the polymer complex of cobalt reflects the process of oxidation of Co(II) into Co(III) which is accelerated by sulfide.

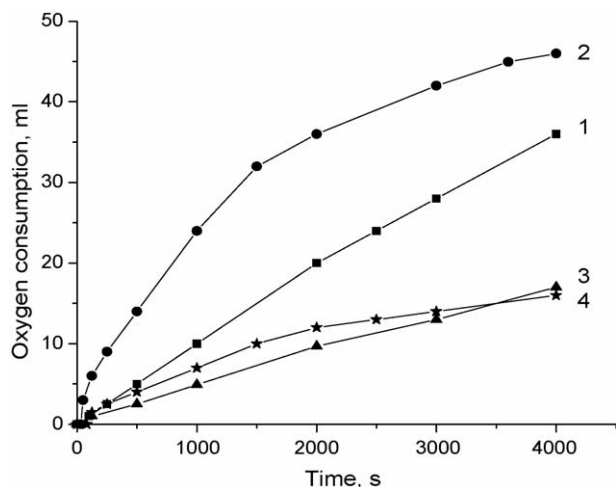


Fig. 1. Kinetic curves of oxygen consumption over time for the catalytic oxidation of sodium sulfide in the presence of: copper complexes with non-prearranged PEI (1); copper complexes with prearranged for copper PEI (2); nickel complexes with prearranged for nickel PEI (3); cobalt complexes with prearranged for copper PEI (4).

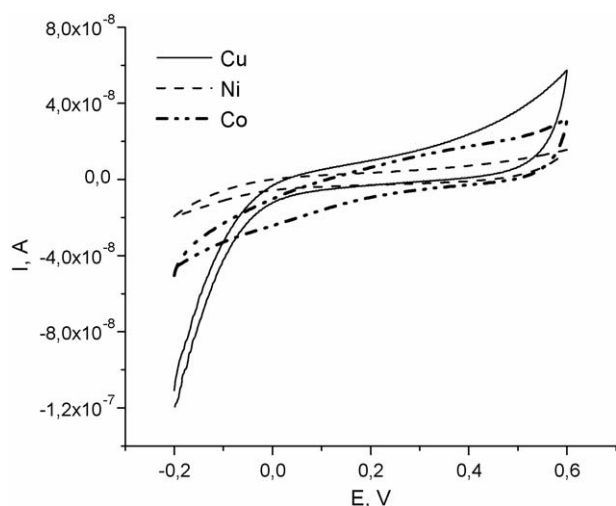


Fig. 2. Voltammograms of non-cross-linked polyethyleimine complexes with copper(II), nickel(II) and cobalt(II) in aqueous borate buffer, pH 10.

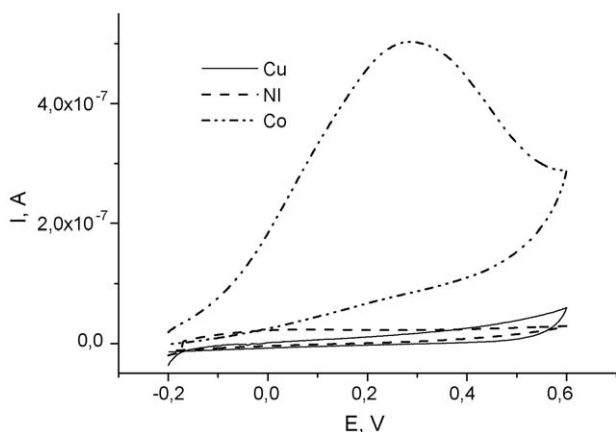


Fig. 3. Voltammograms of non-cross-linked PEI complexes with copper(II), nickel(II) and cobalt(II) in aqueous borate buffer, pH 10, after addition of Na_2S .

4. Conclusion

Prearranged and non-prearranged polymer metal complexes were prepared on the base of poly(ethyleneimine) and *N,N'*-methylenebisacrylamide. The polymer metal complexes were investigated as catalysts in the oxidation of sulfide in aqueous solution. The prearranged polymer Cu(II) complexes exhibit catalytic activity which is comparable with the activity of the commercially employed cobalt(II) phthalocyanine tetrasulfonic acid. Polymer complexes of Ni(II) and Co(II) show a lower catalytic activity. The mechanism of the catalytic oxidation was discussed to explain the different behaviour of the polymer metal complexes. Highly active prearranged Cu(II) complex is a heterogeneous catalyst which is preferable for the reuse of the catalyst.

The results obtained show that complexes of copper with specially prearranged PEI exhibit high catalytic activity in reaction of oxidation of sulfides comparable with that of phthalocyanines but can be easily separated from the reaction media and used repeatedly.

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