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Polymer Chelates of Fe, Co, and Ni Based on 5-Ethynyl-2*H*-tetrazole

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Abstract—Electrochemical preparation of chelates based on 5-ethynyl-2*H*-tetrazole on the surface of iron, cobalt, and nickel results in colored polymer film at low current density. At higher current density the polymer chelate is transferred into the solution. The composition and structure of the polymer chelates has been studied by infrared spectroscopy, elemental analysis, and thermogravimetric analysis. The mechanism of the chelates formation in various solvents has been suggested.

Keywords: electrochemical polymerization, polymer chelate, electrochemical reduction, 5-ethynyl-2*H*-tetrazole

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Metal-polymer materials are widely used in catalysis, medicine, electronics, and other fields of science and engineering [1]. Recently we have performed electrochemical synthesis of chelate of poly-5-vinyltetrazole with iron ions [2]. Accounting for the general interest towards application of polymer derivatives of tetrazole, we have extended the study to investigating the possibility of electrochemical preparation of iron, cobalt, and nickel chelates based on 5-ethynyl-2*H*-tetrazole. The latter contains two sites (N–H and C≡C) potentially active in electrochemical polymerization.

Electrolysis of aqueous, aqueous-ethanolic, and acetonitrile solutions of 5-ethynyl-2*H*-tetrazole at iron, cobalt, or nickel electrode resulted in the formation of the corresponding polymer chelates, when operating in galvanostatic mode at current density $j = 1–30$ mA/cm^2.

The so formed polymer chelates were highly adhesive to the metals, due likely to the formation of some compound at the electrode surface. The surface film grew thicker in the course of electrolysis preventing the tetrazole molecules transport to the electrode surface and the simultaneous release of the metal ions, thus slowing down the overall process. If mechanically detached off the electrode surface, the film cracked upon drying. At lower current density (up to 5 mA/cm^2) the solid uniform film of metallic color was formed; after drying to constant mass the film was insoluble in water and common organic solvents.

At higher current density, the film was no longer uniform, and the polymer chelate was transferred into the solution.

The physical state of hydrated polymer chelates was determined by the concentration of the metal ions in the reaction mixture as well as by temperature. For example, in the case of Co^{2+} chelate the increase in the current density to 15–18 mA/cm^2 (corresponding to increasing Co^{2+} concentration) and cooling of the solution resulted in significant increase in the solution viscosity, and at certain conditions gel could be formed.

In line with the observations made in [3], the dehydration of the films prevented the dissolution of the chelates.

It is known that tetrazolate anions can act either as monodentate or bridging-bidentate ligands, and the metal coordination can occur via nitrogen atom(s) at positions 1 [4–6], 2 [4, 6, 7], 1,2 [8], or 2,3 [9].

Absorption band at 1570 cm^{-1} (typical of bending vibrations of N–H bond) was absent in IR spectra of the polymer chelates. The bands assigned to the aromatic heterocycle (at 1075, 1260, and 1470 cm^{-1})

Selected properties of polymer chelates based on 5-ethynyl-2*H*-tetrazole

Metal	Elementary unit	Color	Content of bound water		Yield with respect to the azole, %	Elemental analysis, found/calculated, wt %		
			calculated, wt%	found (TGA), wt % (°C)		C	N	M
Fe	$(C_3N_4H)_2Fe{\cdot}H_2O$	Dark-brown	6.05	6.7 (140)	91	27.71/27.38	43.1/42.30	21.47/21.38
Co	$(C_3N_4H)_2Co{\cdot}2H_2O$	Light-pink	12.8	12.1 (150)	95	25.63/25.12	39.87/39.18	20.97/20.42
Ni	$(C_3N_4H)_2Ni{\cdot}2H_2O$	Light-blue	12.8	11.9 (155)	90	25.47/24.92	39.61/39.22	20.61/20.15

shifted to lower wavenumbers by 10–30 cm^{-1} upon the complex formation, thus confirming coordination of the metal ions with tetrazolate anions. Shift of the bands assigned to vibrations of terminal acetylene group (2100 and 3290 cm^{-1}) evidenced the interaction of the metal ions with that fragment. Moreover, the presence of the C≡C–H vibration bands in the spectrum demonstrated that it did not participate in electrochemical polymerization. Assignment of the N–H stretching vibrations (2500–3700 cm^{-1}) in the chelates spectra was complicated by the overlap with the bands of bound water.

Taking into account the reference data [2–10] and the results reported here, we suggested that 5-ethynyl-2*H*-tetrazole acted as bridging ligand favoring the formation of polynuclear coordination compounds.

The M–N bond in the polymer chelates was formed via the imine nitrogen atom (N^2), whereas the coordination bond could be formed via the donor-acceptor interaction of the metal ion with the N^3 atom (see Scheme 1). Such structure of the complexes was discussed previously [11, 12].

According to results of TGA and elemental analysis the prepared polymer chelates contained variable amount of bound water, whereas the ligand to metal ratio equaled 2 in all cases (see table).

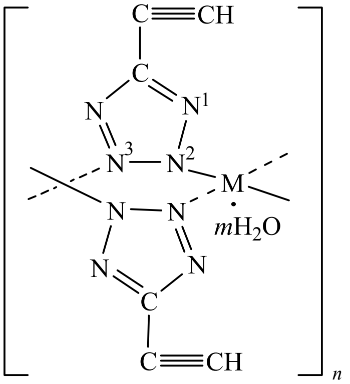
The chelates formation with tetrazole anions in protic (H_2O, MeOH, and EtOH) as well as aprotic (MeCN and DMF) solvents was accompanied with the cleavage of the N–H bond of the heterocycle. If in the protic acids the bond cleavage was due to the interaction with alkali metal ions [13, 14] or with the anions (RO^- or OH^-) formed via cathodic reduction of aliphatic alcohol or water [15, 16], then it is not completely clear why the polymer chelate was formed directly at the anode surface. The complex formation mechanism in the aprotic solvents is not clear as well.

In order to elucidate the complex formation mechanism we studied electrochemical behavior of 5-ethynyl-2*H*-tetrazole in anhydrous acetonitrile in the presence of tetraethylammonium chloride at the metal cathodes (Fe, Co, Ni).

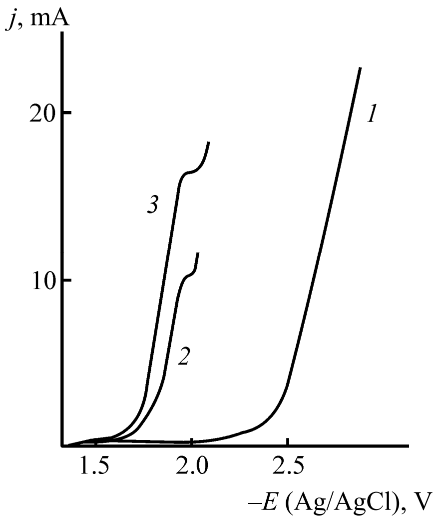
In the polarograms recorded with iron anode (see the figure) a distinct wave of electrochemical reduction of the tetrazole substrate was observed at $-E_{1/2}$ = 1.93–1.95 V, its height increasing with higher concentration of the heterocycle.

In contrast to the cathodes made of non-transition metals (Sn, Cd) or carbon glass, electrochemical reduction of 5-ethynyl-2*H*-tetrazole at Fe, Co, and Ni electrodes was accompanied with intense hydrogen release.

Scheme 1.



M = Fe, Co, Ni; *m* = 1, 2.



Polarograms of electrochemical reduction of 5-ethynyl-2*H*-tetrazole in Et_4NCl solution (0.1 mol/L) in acetonitrile at iron cathode. Concentration of 5-ethynyl-2*H*-tetrazole, mol/L: (*1*) 0, (*2*) 2×10^{-2}, and (*3*) 5×10^{-2}.

Basing on the collected data, we suggest the following scheme of formation of polymer chelates based on 5-ethynyl-2*H*-tetrazole in aprotic solvents at cathode of transition metal M.

$$\text{Anode } M - 2\bar{e} \rightarrow M^{2+},$$

$$\text{Cathode } 2{>}N{-}H + 2\bar{e} \rightarrow 2{>}N^{-} + H_2,$$

$$\text{Overall } nM^{2+} + 2n{>}N^{-} \rightarrow [M({>}N)_2]_n.$$

Hence, similarly to pyrazole [13, 17] and triazole [18], 5-ethynyl-2*H*-tetrazole underwent electrochemical reduction with the rupture of the N–H bond in anhydrous aprotic solvents at the transition metal cathode.

The process occurred differently in protic solvents (H_2O, MeOH, and EtOH). For instance, in the course of 5-ethynyl-2*H*-tetrazole electrolysis in 0.1 mol/L aqueous solution of Et_4NCl and LiCl in the cell equipped with the cation exchange membrane (5-ethynyl-2*H*-tetrazole was present in both parts of the chamber) the polymer chelate was formed only in the anodic chamber. Probably, 5-ethynyl-2*H*-tetrazole was adsorbed at the metal surface, and then dehydrated to form the polymer chelate. Alternatively, the oxidation of 5-ethynyl-2*H*-tetrazole could give the cation-radicals interacting with the anode material.

EXPERIMENTAL

Polarography measurements were performed using the P-5827M potentiostat and the PI-50-1 pulse potentiostat in the glass cell with working volume of 20 mL equipped with the cooling contour. The studied metal plate (Fe, Co, or Ni) acted as cathode; the auxiliary electrode was made of platinum; the reference electrode was a plate immersed into solution of background electrolyte (0.09 V in 0.1 mol/L solution of Et_4NCl in MeCN relative to saturated silver chloride electrode). Contact of the latter with the working electrode was organized via the electrolytic bridge.

Acetonitrile was purified by boiling and distillation over $KMnO_4$ and CaH_2.

5-Ethynyl-2*H*-tetrazole was prepared and recrystallized from anhydrous ethanol as described elsewhere [19]. Anhydrous solvents were prepared via standard methods [20]. The obtained polymer chelates were twice recrystallized from anhydrous ethanol and water, and then dried under reduced pressure (1 mmHg, 80°C, 2 h).

IR spectra were recorded using the sample in the form of KBr pellets or thin film of suspensions in mineral oil. Thermogravimetry analysis was performed using the MOM derivatograph (Paulik–Paulik–Erdey).

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