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Binary and Ternary Copper(II) Complexes with NIPAAm/IA Copolymers and Aminoacids: Interpretation of UV-Visible Spectra and Cyclic Voltammograms

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The complex formations of homopolymers and copolymers of poly(N-isopropyl acrylamide) (PNIPAAm), polyacrylamide (PAAm) and poly(itaconic acid) (PIA) with Cu(II) ions in aqueous solutions were studied by using UV-visible spectra in the region of 200–1100 nm and cyclic voltammograms between −0.800 V and 0.600 V. According to the optical and electrochemical spectra of the polymer- and copolymer-Cu(II) complexes and their ternary complexes with alanine, i.e., absorptions and the shifts in the wavelength of the maximum absorptions, currents and potentials of the peaks in the pH range of 3–12, the intensities of anodic and cathodic peak currents of polymers containing IA groups decrease with increasing pH and they show maximum absorptions at lower wavelengths than do the homopolymers used in this work. The peak point of the visible band shifts from 800 to 650 nm, with increasing pH, while the intensity of the third anodic peak observed after pH = 4 increases in the case of both Ala-Cu(II) and its ternary solution with P(NIPAAm-co-IA, 9.8 mol%). Both the pH-dependent shifts of maximum absorptions and the appearence of the third anodic peaks as the pH raised were interpreted as a presence of tetracoordinated Cu(II) complexes in the solution and on the electrode surface, involving combined carboxyl, amide and amine interaction.

Keywords: poly(N-isopropyl acrylamide); poly(itaconic acid); polymer-copper(II) complexes; ternary complexes; cyclic voltammetry; UV-visible spectroscopy.

1 Introduction

Polymer-metal complexes play an important role in biological applications and chemical industries such as protein-supported metal complexes, hydrometallurgy, wastewater treatment, and nuclear chemistry (1–4). Biochemical effects of enzymes and coenzymes that contain metals (cobalt, copper, iron, zinc and molybdenum), metal-containing vitamins and metalloproteins have been studied extensively (5–7). The therapeutic effectiveness of metal complexes with various biologically active ligands has been shown by experimental and clinical research (8–10). This biological action depends on their reaching the target organs and the rate of release of the metal from the complex. Furthermore, immunological properties of complexes of proteins with polyelectrolytes bearing essential functional groups such as antigen-binding ligands have been studied systematically (11–15).

Spectroscopic and electrochemical studies show that certain inorganic metal ions such as Ni(II), Fe(II), Cu(II), Zn(II) and Cd(II) coordinate with polymeric chelating agents (polychelatogens) through ionic bonds, coordination bonds and ion-dipole interactions to form polymer-metal chelates. In addition, it is known that the nature and content of organic functional groups on polymeric ligands, neutralization degree in the case of polyelectrolytes, ionic strength and pH of the solvent/solution influence the structures of the complexes formed (16–19).

Linear polymers and hydrogels of N-isopropyl acrylamide, NIPAAm exhibit a sharp phase transition from hydrophilic to hydrophobic structure at its lower critical solution temperature, LCST which is close to the body temperature (32–34°C). When NIPAAm is copolymerized so as to obtain the right balance of hydrophobic and hydrophilic monomers, its LCST can be manipulated (20–23). The concept of using PNIPAAm as the main polymeric chelating agent in this study is of interest for biological applications such as controlled or targeted drug release, immobilization of enzymes (24, 25). From a starting point of view, we have studied the systems PNIPAAm/Cu(II), polyacrylamide (PAAm)/Cu(II), P(NIPAAm co-itaconic acid) P(NIPAAm-co-IA)/Cu(II), P(NIPAAm-co-acrylic acid) P(NIPAAm-co-AA)/Cu(II) and P(AAm-co-IA)/Cu(II) and, their ternary complexes with Alanine (Ala) because ternary coordination complexes

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had an important role in biological processes, as exemplified by many instances in enzymes, were known to be activated by metal ions (9, 11). Ala, $CH_3CH(NH_2)COOH$, found in many proteins and containing a methyl group on the α-carbon atom was chosen as a model component to interpret the interactions between proteins and water soluble polymers with ionizable side groups in the presence of Cu(II). In addition, valine (Val), $(CH_3)_2CHCH(NH_2)COOH$, bearing hydrophobic isopropyl group on the α-carbon atom and so having asimilar structure with NIPAAm were used to prepare Val/Cu(II) complexes and to study the effect of hydrophobicity on metal-complex formation by means of cyclic voltammetry. IA, AA and PIA were chosen as ionic comonomers and polyacid, respectively. IA and AA have two and one carboxyl groups, and they are known to form a complex with divalent metal ions (26–29). PAAm contains numerous amide groups, which can interact with ions of the solution through the complex formation between them and hydrated ions (30–32). It was chosen as a model matrix to observe the complex formation efficiency of hydrophobic isopropyl groups of PNIPAAm. Optical properties and electrochemical behavior of the complexes obtained with various combinations of polymer, copolymer and amino acid molecules in the presence of Cu(II) ion have been investigated by means of spectroscopic and voltammetric measurements.

2 Experimental

PNIPAAm, PAAm, PIA and, P(NIPAAm-co-IA), P(NIPAAm-co-AA) and P(AAm-co-IA) copolymers containing 9.8 and 10.0 mol% IA and AA, respectively, were prepared via free radical polymerization using potassium persulfate ($K_2S_2O_8$) in distilled-deionized water at 50°C in a nitrogen atmosphere. The homopolymerization of NIPAAm and the copolymerization of the mixture containing 10 mol% AA in the feed were continued for 2 h, while the homopolymerization of IA and the copolymerization of NIPAAm and IA were allowed to proceed 48 and 24 h, respectively. Purification and characterization of homo- and copolymers of AAm, NIPAAm and IA have been reported in our previous articles (23, 33). $CuSO_4 \cdot 5H_2O$, Ala and Val were all of reagent grade purity (Merck) and were used without further purification.

The spectrophotometric and voltammetric studies were carried out for the following systems: (a) Cu(II)-Ala and Cu(II)-Val; (b) Cu(II)-PIA; (c) Cu(II)-PNIPAAm; (d) Cu (II)-PAAm; (e) Cu(II)-P(NIPAAm-co-IA); (f) Cu(II)-P(NIPAAm-co-AA) (g) Cu(II)-P(AAm-co-IA) and (h) their ternary complexes with Ala. Absorption spectra were obtained with a Shimadzu UV-VIS 160A spectrophotometer, equipped with a temperature controlled cell. All the samples were prepared by mixing the solutions of the interacting components at least one hour before measurements. Cyclic voltammograms (CV) were obtained by using a model 2263 Parstat potentiostat. A platinum wire $3.14 \times 10^{-2}\,cm^2$ area was used as working electrode. The reference and auxiliary electrodes were saturated calomel and Pt wire, respectively. All experiments were carried out at room temperature and in deoxygenated medium, by passing nitrogen gas through the solution for 20 min.

The concentrations of polymers were calculated considering the molar mass of the repeating units. Distilled-deionized water was employed in preparation of solutions. The stock solution of metal ion was prepared in water at $pH = 3$ to prevent the precipitations at higher pHs. For the synthesis of polymer-metal complexes and ternary complexes, the unit mole ratios of polymer to $CuSO_4 \cdot 5H_2O$, i.e., $r = n_{polymer}/n_{metal\ salt}$ were changed from 50 to 4, where $n_{polymer}$ and $n_{metal\ salt}$ are the mole number of ligands and Cu(II) ions per mL of solutions, respectively. The pH values between 2.0–12.0 of the solutions were adjusted by adding HCl and NaOH solutions, for all spectrophotometric and voltammetric measurements.

3 Results and Discussion

In the literature, complex formation between the active groups of water soluble polymers such as PAAm, PEG, PNIPAAm (neutral polymers) and PAA, PMAA (anionic polymers), i.e., interpolymer complexation and the complexation of these polymeric ligands containing anchoring sites like nitrogen and oxygen with metal ions have been studied using various spectroscopic methods and electroanalytical techniques (18, 34–37). The stability of the complexes in the cases of PNIPAAm and PMAA have been attributed to the presence of hydrophobic isopropyl and methyl side groups, respectively. In our present investigation, the effect of addition of hydrophobic isopropyl groups on to the amide groups of PAAm and hydrophilic carboxyl groups attached to α-carbon atoms of PAA on the interaction mechanisms between PNIPAAm, PIA and their copolymers with Cu(II) ions were examined using UV-visible spectrophotometer and a standard three electrode system. These spectrophotometric and voltammetric results were compared with the ones obtained by the interaction of PAAm, P(AAm-co-IA), P(NIPAAm-co-AA), Ala and Val with Cu(II) ions to observe the influence of increasing hydrophobicity and hydrophilicity on the complexation mechanisms. The results of all spectroscopic measurements in the visible region in the range of 400–1100 nm and voltammetric behavior between −0.800 V and 0.600 V are given in Tables 1–5.

It is known that the structural environment of a ligand, which is connected on a polymer chain, along with chemical structure, affects the stability and geometryof its metal complexes (19). Therefore, the metal-complex formation of small molecules is made in order to identify the polymer-metal compounds. In this study, Ala and Val (for some voltammetric measurements), being two of the repeating units in the protein molecules, were used as the model compounds to interpret the structures of binary and/or

Table 1a. Maximum absorptions and wavelengths obtained from visible spectra of Ala-Cu(II) and homopolymer-Cu(II) complexes

	Ala		PNIPAAm		PAAm		PIA	
pH	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.
3	788	0.046	800	0.019	—	—	827	0.026
4	756	0.063	780	0.020	760	0.056	729	0.108
5	740	0.080	778	0.021	716	0.076	729	0.121
6	636	0.115	778	0.023	691	0.090	719	0.123
7	607	0.133	739	0.047	685	0.107	722	0.116
8	615	0.123	—	—	691	0.138	—	—
9	617	0.124	755	0.048	—	—	729	0.108
10	617	0.123	—	—	691	0.146	726	0.103
11	—	—	—	—	—	—	—	—
12	644	0.085	—	—	—	—	—	—

ternary complexes of water soluble copolymers containing carboxylic acid and amide side groups, in the presence of Cu(II) ions. It has been demonstrated previously by various researchers that the UV-Vis spectra of Cu(II) in aqueous glycine solutions were highly sensitive to pH and glycine concentration and the molecule has formed a five membered chelate ring, being composed of the molar ratio 1:2 of Cu(II) to glycine (38–40). In preparation for the interpretation of visible spectra and cyclic voltammograms (CV) of Cu (II)-P(NIPAAm-co-IA, 9.8 mol%), the spectra in the visible region and CVs of cupric ion in aqueous Ala and Val solutions were examined. The results obtained with the cupric ion in 0.0133 mol/L Ala and Val (in 0.1 mol/L KCl solution, in the case of CV measurements) over the pH region of 3 to 11 are shown in Figures 1a–c and in Tables 1, 2a, 2b. The mole ratios of Ala and Val to $CuSO_4$, i.e., $r = n_{Ala(orVal)}/n_{Cu(II)}$ were adjusted to 4.00 and 6.67 for spectroscopic and voltammetric measurements, respectively. When the acidic solutions of Ala-Cu(II) investigated ($pH \leq 6$), it seems that the repulsion of positively charged of the amino acid nitrogen, NH_3^+- $CH(CH_3)COO^-$ for the cupric ion is enough to decrease the affinity of the carboxyl group. As

Table 1b. Maximum absorptions and wavelengths obtained from visible spectra of copolymer-Cu(II) complexes

	P(AAm-co-IA)		P(NIPAAm-co-IA)	
pH	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.
3	—	—	782	0.063
4	722	0.045	772	0.083
5	698	0.098	753	0.100
6	679	0.110	726	0.151
7	679	0.105	716	0.146
8	679	0.102	712	0.142
9	679	0.100	695	0.132
10	679	0.098	688	0.141
11	—	—	665	0.141
12	—	—	649	0.152

Table 2a. Changes in the anodic peak currents and shifts in the peak potentials with increasing pH of amino acid-Cu(II) complexes

	Cu(II)		Alanine + Cu(II)		Valine +Cu(II)	
pH	E_{aII}, V	I_{aII} (μA)	E_{aII}/E_{aIII}, V	I_{aII}/I_{aIII}, (μA)	E_{aII}, V	I_{aII} (μA)
3	−0.087	35.2	−0.070	41.3	−0.089	46.5
4	−0.098	25.2	−0.072	38.6	−0.100	32.7
5	−0.104	19.2	−0.098	32.5	−0.120	19.5
6	−0.117	15.3	−0.078	21.9	−0.123	14.0
			−0.232[a]	7.8[a]		
7	—	—	−0.033	19.6	−0.170	14.3
			−0.218[a]	10.9[a]		
8	—	—	−0.025	15.4	−0.151	13.5
			−0.212[a]	9.8[a]		
9	—	—	−0.032	11.8	−0.176	12.6
			−0.220[a]	11.3[a]		
10	—	—	—	—	−0.207	2.8
			−0.218	8.8		

[a] Anodic peak formed after pH 5.

Table 2b. Changes in the cathodic peak currents and shifts in the peak potentials with increasing pH of amino acid-Cu(II) complexes

	Cu(II)		Alanine + Cu(II)		Valine +Cu(II)	
pH	E_{cII}, V	I_{cII} (μA)	E_{cII},V	I_{cII} (μA)	E_{cII}, V	I_{cII} (μA)
3	−0.316	18.9	—	—	—	–
4	−0.277	18.0	−0.326	26.3	−0.300	21.8
5	−0.325	17.4	−0.275	18.7	−0.178	13.9
6	−0.338	16.1	−0.219	7.4	−0.197	11.6
7	—	—	−0.212	8.8	−0.150	8.7
8	—	—	−0.232	8.0	−0.210	10.9
9	—	—	−0.209	8.5	−0.224	9.1
10	—	—	−0.245	8.9	−0.300	7.9

Table 3a. Changes in the intensities of peak currents and shifts in the peak potentials with increasing pH of polymer-Cu(II) complexes

	Cu(II)		PNIPAAm + Cu(II)		Cu(II)		PNIPAAm +Cu(II)	
pH	E_{aII}, V	I_{aII} (μA)	E_{aII}, V	I_{aII} (μA)	E_{cII}, V	I_{cII} (μA)	E_{cII}, V	I_{cII} (μA)
3	−0.050	36.6	−0.050	30.8	−0.250	12.1	−0.250	9.4
4	−0.050	30.4	−0.050	20.1	−0.250	11.5	−0.220	11.9
5	−0.060	24.1	−0.050	18.6	−0.270	11.5	−0.250	10.9
6	−0.050	22.6	—	—	−0.250	10.9	—	—
7	0.000	2.1	−0.100	2.1	−0.400	6.6	−0.300	6.4

Table 3b. Changes in the intensities of the peak currents and shifts in the peak potentials with increasing pH of polymer-Cu(II) complexes

	Cu(II)		P(NIPAAm-co-IA) + Cu(II)		Cu(II)		P(NIPAAm-co-IA) + Cu(II)	
pH	E_{aII}, V	I_{aII} (μA)	E_{aII}, V	I_{aII} (μA)	E_{cII}, V	I_{cII} (μA)	E_{cII}, V	I_{cII} (μA)
3	−0.078	45.7	−0.128	24.5	−0.274	17.9	−0.285	7.5
4	−0.099	30.3	−0.134	10.8	−0.283	18.1	−0.298	6.4
5	−0.107	22.5	−0.144	4.4	−0.216	12.6	−0.564	7.1
6	−0.124	18.5	—	—	−0.223	14.9	−0.408	6.9
7	−0.005	4.1	—	—	−0.360	10.8	—	—

the pH raised, the maxima of visible spectra of Cu(II)-Ala complexes shift to shorter wavelengths and to higher absorptions. This shift is parallel with the ease of removal of a hydrogen ion from NH_3^+-, as the pH increased. Therefore, it indicates that the cupric ion is bound in the complex through the amine group and the formation of Cu(II).... NH_2- bond facilitate the complex formation with carboxyl group because of attraction between anionic COO^- and cationic metal (Figure 1a). In addition, these complex formations are supported by cyclic voltammetric measurements (Figures 1b and 1c). From analysis of the changes in the peak currents and the shifts in the peak potentials in Tables 2a and 2b and in Figures 1b and 1c, it was observed that as the pH increased the anodic peak potential (E_{aII}) of Val-Cu(II) system was regularly shifted towards more negative values. Furthermore, in the case of Ala-Cu(II) system a new peak (*E_{aIII} in Table 2) appeared as a more negative potential than E_{aII} and around pH 5 while the second anodic peak, E_{aII} shifted to more positive values and its intensity decreased. The potential values of the third anodic peak were nearly constant but intensity increased with an increase in pH. Both this new peak produced in the anodic region by Ala-Cu(II) ($CH_3CH(NH_2)COOH$-Cu(II)) system after pH 6 and E_{aII} of Val-Cu(II) ($(CH_3)_2CHCH(NH_2)COOH$) system in the pH range of 3−10 were ascribed mainly to the

Table 4a. Maximum absorptions and wavelengths of Ala-Cu(II)-homopolymer ternary complexes obtained from visible spectra

	PNIPAAm		PAAm		PIA	
pH	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.
3	778	0.053	—	—	768	0.059
4	725	0.083	693	0.150	733	0.083
5	684	0.111	632	0.186	714	0.100
6	638	0.135	625	0.222	714	0.104
7	626	0.158	619	0.217	668	0.100
8	—	—	619	0.217	—	—
9	617	0.178	—	—	643	0.097
10	617	0.173	620	0.191	645	0.101
11	619	0.163	—	—	—	—

Table 4b. Maximum absorptions and wavelengths of Ala-Cu(II)-copolymer ternary complexes obtained from visible spectra

	P(AAm-co-IA)		P(NIPAAm-co-IA)		P(NIPAAm-co-AA)	
pH	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.	λ_{max}, nm	Abs.
3	—	—	787	0.045	792	0.056
4	681	0.169	751	0.077	750	0.083
5	662	0.209	705	0.108	694	0.110
6	612	0.243	665	0.116	640	0.142
7	610	0.256	647	0.125	620	0.161
8	612	0.175	626	0.126	—	—
9	613	0.156	626	0.120	623	0.171
10	611	0.146	626	0.110	624	0.165
11	—	—	—	—	—	—

Table 5. Changes in the intensities of the peak currents and shifts in the peak potentials with increasing pH of ternary complexes

	Cu(II)		P(NIPAAm-co-IA) + Cu(II) + Alanine		Cu(II)		P(NIPAAm-co-IA) + Cu(II) + Alanine	
pH	E_{aII}, V	I_{aII} (μA)	E_{aII}, V	I_{aII} (μA)	E_{cII}, V	I_{cII} (μA)	E_{cII}, V	I_{cII} (μA)
3	−0.066	54.4	−0.074	63.0	−0.296	19.6	−0.269	17.5
4	−0.082	39.9	−0.086	54.0	−0.318	18.3	−0.282	16.0
5	−0.092	27.0	−0.101	40.0	−0.325	13.4	−0.543	19.8
6	−0.135	7.9	−0.087	30.0	−0.547	9.1	−0.591	18.1
7	—	—	−0.060	25.0	—	—	−0.600	19.4

adsorption of Ala-Cu(II) and Val-Cu(II) complexes on the electrode surface. In addition, E_{aII} (in the case of Ala) and E_{cII} (both Ala and Val) shifted more positive values according to the anodic and cathodic peaks of copper were evaluated as a sign of the existence of stable metal-polymer complexes in solution. As a summary, it can be said that in the pH range of 3–5, the protonated amino acid complex is the only one of the species while in an alkaline solution i.e., pH 6 to pH 10, the deprotonated amino acid complex is formed. In the second case, both carboxyl and amino groups are coordinated with copper ions and, some of these tetra co-ordinated Cu (II) complexes formed in solution may be adsorbed on the electrode surface because of hydrophobic methyl and isopropyl groups of Alanine and Valine, respectively. On the other hand, in the strongly acidic region (pH = 3–5) most of the Cu(II) ions are coordinated only by water molecules, though there must be some interaction between Cu(II) ions and COO^- groups.

To interpret the dependence of structures of polymer-metal complexes in aqueous solutions on the nature of the ligand, the absorptions and the shifts in the wave length of the maximum absorptions in the optical region of 400–1100 nm and in the pH range of 3–12 of PNIPAAm and P(NIPAAm-co-IA) were compared with the ones of PAAm and P(AAm-co-IA), respectively.

Visible spectra of aqueous solutions of P(AAm-co-IA, 9.8% in mole) and P(NIPAAm-co-IA, 9.8% in mole) at different pH values are shown in Figures 2 and 3, respectively. From the results summarized in these Figures and Table 1, it can be seen that it is interesting to study the composition and structure of copper complexes of the copolymers, in which the strongly coordinating carboxyl groups are

Table 6. Anodic peak currents and potentials of binary and ternary complexes

	Cu(II)		P(NIPAAm-co-IA) + Cu(II)		Alanine-Cu(II)		P(NIPAAm-co-IA) + Alanine + Cu(II)	
pH	E_{aII}, V	I_{aII} (μA)	E_{aII}, V	I_{aII} (μA)	E_{aII}/E_{aIII^a},V	I_{aII} (μA)	$E_{aII}/E_{aIII}{}^a$ V	I_{aII} (μA)
3	−0.078	45.7	−0.128	24.5	−0.070	41.3	−0.074	63.0
4	−0.099	30.3	−0.134	10.8	−0.072	38.6	−0.086	54.0
5	−0.107	22.5	−0.144	4.4	−0.098	32.5	−0.101	40.0
							-0.277^a	5.9^a
6	−0.124	18.5	—	—	−0.078	21.9	−0.087	30.0
					-0.232^a		-0.242^a	9.1^a
						7.8^a		
7	−0.005	4.1	—	—	−0.033	19.6	−0.060	25.0
					-0.218^a		-0.218^a	10.1^a
						10.9^a		
8	—	—	—	—	−0.025	15.4	−0.067	26.8
					-0.212^a		-0.222^a	12.2^a
						9.8^a		
9	—	—	—	—	−0.032	11.8	−0.032	7.2
					-0.220^a		-0.187^a	5.0^a
						11.3^a		
10	—	—	—	—	—	—	0.005	13.4
					−0.218	8.8	-0.200^a	13.3^a

[a] Anodic peak formed after pH 4.

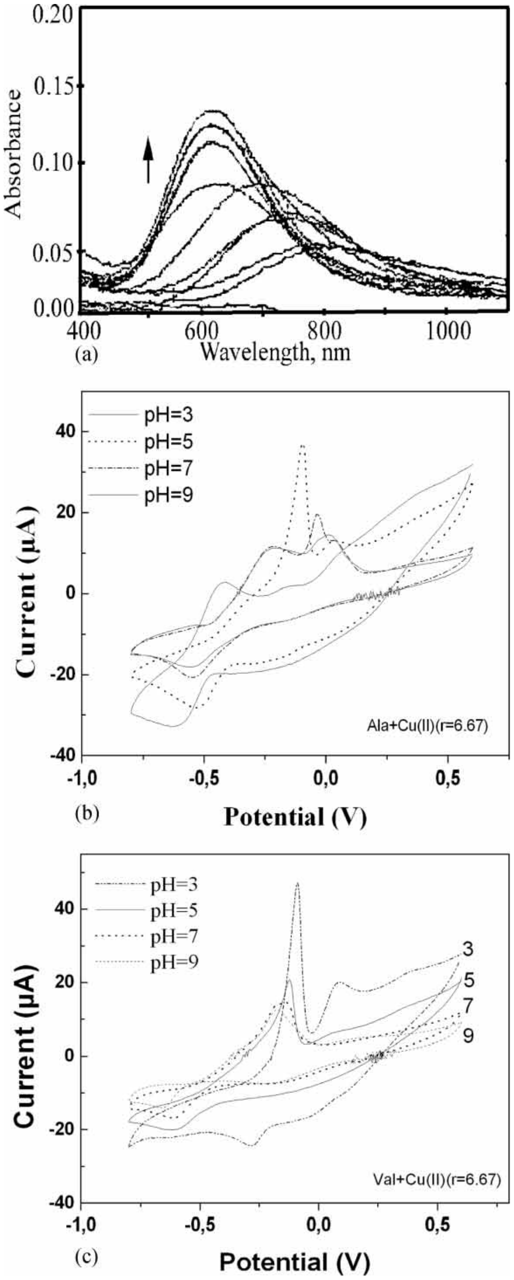


Fig. 1. (a) Visible spectra of aqueous Cu(II)-Alanine solutions at r = 4 and in the region of pH = 3–12. The increasing in pH are marked by the arrow. (b) Cyclic voltammograms of Cu(II)-Alanine solutions at four different pH: 3.0; 5.0; 7.0 and 9.0. Supporting electrolyte 0.1 M KCl and the scan rate is 100 mV/s. (c) Cyclic voltammograms of Cu(II)-Valine solutions at four different pH: 3.0; 5.0; 7.0 and 9.0. Supporting electrolyte 0.1 M KCl and the scan rate is 100 mV/s.

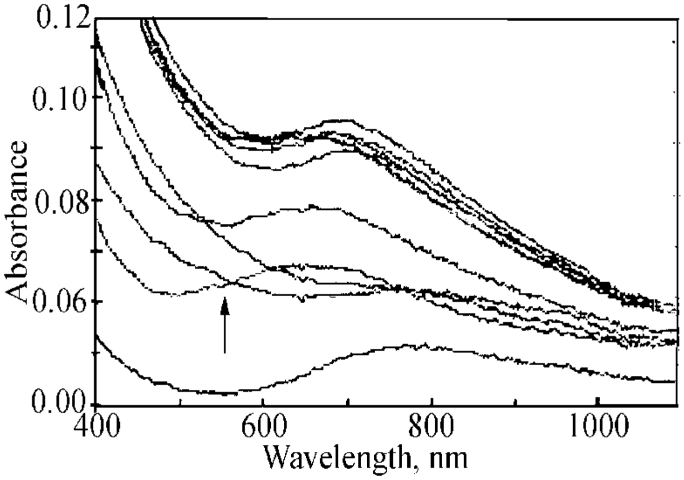


Fig. 2. Visible spectra of aqueous P(AAm-co-IA)-Cu(II) solutions at r = 4 as a function of pH. The pH order between 4–10 are marked by the arrow.

disrupted by several neutral and so weakly complex forming units such as AAm and NIPAAm. These repeat units have two potential complexation donor atoms (oxygen and nitrogen) available for chelate formation. The main difference between them is the presence of a hydrophobic and bulky group bound onto the nitrogen atom in the case of NIPAAm. According to the maximum absorption values observed, PAAm and PNIPAAm homopolymers yield binary complexes containing Cu(II) ions and chelated with N and O atoms attached to the polymer (Scheme 1a). However, from the practically negligible increase in absorptions (especially in the case of PNIPAAm) over that of $CuSO_4 \cdot 5H_2O$ (for example, 0.018 and 0.045 at pH 3 and pH 7, respectively) (Table 1), it is apparent that very little Cu(II) has formed a complex with the amide groups of PAAm and PNIPAAm. From these results, it can be seen that the hydrophobic and bulky isopropyl groups reduce the affinity of the PNIPAAm chains for cupric ion. Further, the pH- independent absorptions are directly related to their neutral molecular structures. In the case of the electrochemical spectrum obtained by cyclic voltammetry, the absence of additional anodic peak assumed to the adsorption of polymer-metal complex and the constancy of peak potentials but slightly decreased anodic peak currents also supported that only small part of the isopropyl groups attached to the main chain of PNIPAAm could formed complexes with Cu(II) ions in the solution (Table 3a).

Visible spectra of aqueous solutions of P(NIPAAm-co-IA, 9.8% in mole) containing various concentrations of Cu(II) are shown in Figure 4. The absorption maxima at pH 6 were seen around 700 nm and the absorbance increased with a decrease in mole ratio of copolymer to Cu(II) from 50 to 4. From these data on spectra, it can be said that cupric ion complexes with carboxylate and amide groups in the copolymer chains do not have an important absorption peak above 700 nm. Furthermore, it means that in the other cases, i.e., at high ratios of r ($n_{polymer}/n_{metal\ salt}$) and at low pH's, most of the Cu(II) ions are coordinated only water molecules.

From the comparison of the data obtained for polymer-metal complexes with the ones by the addition of alanine, it was observed that maximum absorptions close to 700 nm (pH = 6) increased and their maximum values regularly

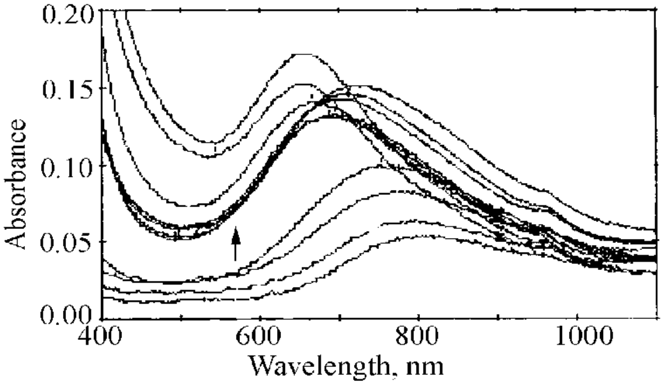


Fig. 3. Visible spectra of aqueous P(NIPAAm-co-IA)-Cu(II) solutions at r = 4 as a function of pH. The pH order between 3–12 are marked by the arrow.

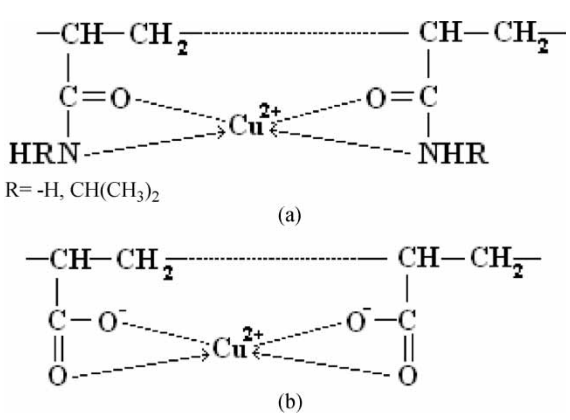
shifted to lower wavelengths with increasing pH, for $n_{\text{Ala+-Polymer}}/n_{\text{Cu(II)}} = 4$. P(NIPAAm-co-IA, 9.8 mol%)-Cu(II)-Ala ternary system had peaks at lower wavelengths than do the P(NIPAAm-co-IA, 9.80 mol%)-Cu(II) system for the same pH region (especially after pH = 5, corresponding izoelectric point of amino acid molecule) (Figure 5). It is already known from the literature that all copper proteins at pHs above 7 have been found to absorb light in the region of 600 nm, which indicates a behavior that the copper is tetracoordinated and that at least two bonds are of the amine type.

According to both our findings and literature results, we can assume that a tetracoordinated Cu(II) complex for the ternary system of P(NIPAAm-co-IA, 9.8% in mole)-Cu(II)-Ala, involving combined carboxyl, amide and amine interaction will be possible with a structure as follows (Scheme 2).

The ternary complexes of all other polymers used in this work, except PIA showed similar behaviors in the visible region (Table 4). The strongly shifted wave lengths of maximum absorptions and their positions between pH 5 and pH 7 are quite characteristic of the results obtained with Cu(II) complexes with simple amines and with polypeptides.

Thus, it is seen that there is strong evidence that at pH's, which are sufficiently high for the removal of a hydrogen ion from NH_3^+–, Cu(II) ion, will form a complex with amine groups of amino acid molecules (Figures 1, 5 and Scheme 2). This means that in the case of the ternary complexes, absorption maxima are in a region characteristic of Cu(II)-NH_2 type linkage, whereas in the polymer-Cu(II) complexes, the effect of Cu(II) ions is different from that of the ternary complexes. In the latter case, the smooth shiftings and increases in the whole pH region indicate the presence of amide and carboxylate complexes, which become greater as the pH is increased (Scheme 1). The peak potentials and currents obtained from cyclic voltammograms of the solutions of binary and ternary complexes were compared by spectroscopic data in the visible region (Tables 3b, 5, 6, and Figure 6). In the case of the P(NIPAAm-co-IA, 9.8 mol%)-Cu(II) system, the decrease of anodic and cathodic peak currents pointed to the existence of polymer-metal complexes in solution, while for the P(NIPAAm-co-IA, 9.8 mol%)-Cu(II)-Ala system, the presence of an additional anodic peak observed after pH 4, along with the second anodic peak and the similarity of the voltammetric behavior of the ternary system and Ala-Cu(II) solutions supported the discussion, which has been done according to the spectrophotometric behavior in the visible region. This indicated that the metal complexes in these solutions (and on the electrode surface for the ternary system) were formed by carboxylate, amide, and amine interactions.

Polymers and copolymers of acrylic acids and its derivatives, amines, and amides are widely used as macroligands (41, 42). It is reported that the average coordination number of PAA-metal complexes varies from zero to more than 2, depending on the solution pH and the concentration ratio of PAA to the metal ions (43–47). At high pH values, the PAA chain has a stretched shape due to electrostatic repulsion of charged carboxylate groups. In this case, metal ions are complexed, either with one or two neighbor groups. At a



Sch. 1. Structures of binary complexes: (a) PAAm-Cu(II); PNIPAAm-Cu(II) (amide type complexes) and (b) PIA-Cu(II) (carboxylic type complexes).

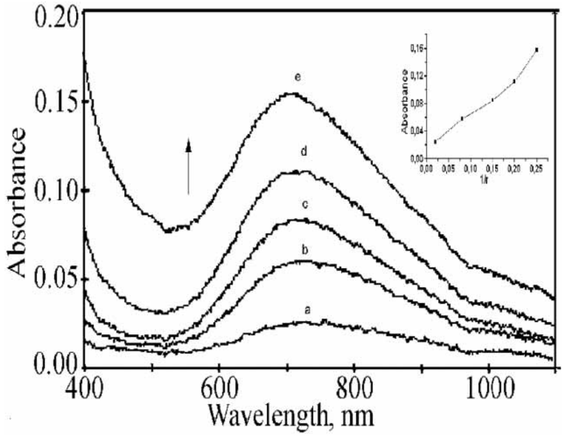


Fig. 4. Visible spectra of aqueous P(NIPAAm-co-IA)-Cu(II) solutions at various $n_{\text{polymer}}/n_{\text{Cu(II)}}$ ratios, r: (a) 50.0, (b) 12.5, (c) 6.7, (d) 5.0 and (e) 4.0. The pH is kept constant at 6.

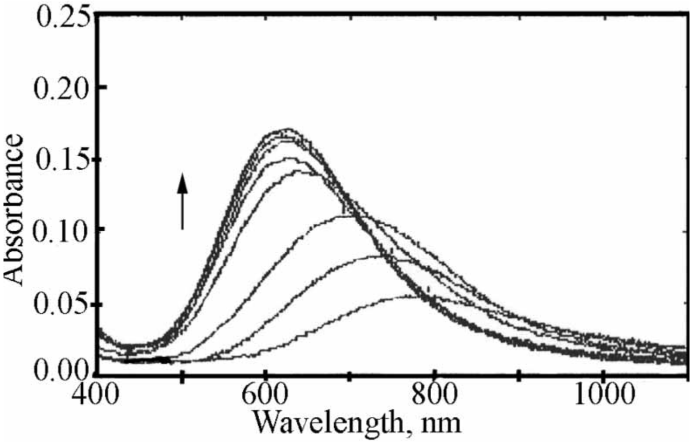


Fig. 5. Visible Spectra of aqueous P(NIPAAm-co-IA)-Cu(II)-Ala ternary solutions at r = 4 as a function of pH. The pH order between 3–10 are marked by the arrow.

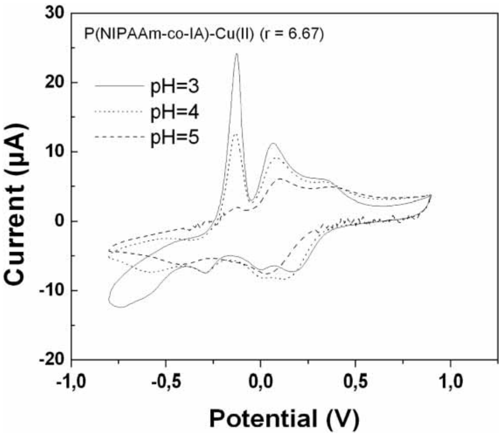
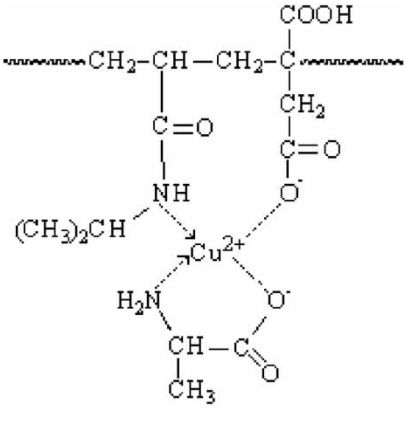


Fig. 6. Cyclic voltammograms of P(NIPAAm-co-IA)-Cu(II) binary solutions at three different pH: 3.0, 4.0, and 5.0. Supporting electrolyte 0.1 M KCl and the scan rate is 100 mV/s.

pH value, being lower than 4, the macromolecular globule contracts and the metal ions are able to coordinate 2–4 carboxyls. Pizarro et al. have reported the Cu(II) binding properties of poly(phenylmaleimide-co-β methyl hydrogen itaconate) and poly(phenylmaleimide-co-acrylic acid). According to their findings, the β-carbonyl group of itaconate cannot interact with the metal ion to form a stable complex because of steric hindrance. The interaction of the imide and carboxylic groups with metal ions can lead to the formation of stable molecular complexes between the electron-donor nitrogen of imide and the carbonyl groups of acrylic acid (48). It is known that amino groups form stable complexes through the free electron pair from the nitrogen atom. As a result, the stability of the complexes depends strongly on the pH. At low pH, where the majority of the amino groups are protonated, the affinity by the metal ions is poor and the stability of the complex is low (Scheme 3). As the pH increases, the affinity and stability of the polymer–metal complexes increases (42).



Sch. 2. Structure of P(NIPAAm-co-IA, 9.80 mol%)-Cu(II)-Ala ternary complex.

In the cases of PIA-Cu(II) and PIA-Cu(II)-Ala complexes we observed different behaviors than the others in the same pH region, except the absorption value of PIA-Cu(II) complexes at pH 3. This absorption value and its maximum wavelength, being approximately equal to that of $CuSO_4 \cdot 5H_20$ (0.023 and 828 nm, respectively) indicate that Cu(II) ions are coordinated only by water molecules because it is known that at pH ≤ 3, itaconic acid has a molecular form. With increasing pH from 3 to 4, the visible band shifted from 800 to 730 nm and the absorption intensities increased in their approximately maximum values, in the case of PIA-Cu(II) complexes. These effects can be explained by nearly completed complexation of deprotonated free carboxyl groups and Cu(II) ions and, all complexation centers in the solution are used in the formation of polymer-metal complexes (Scheme 1). The precipitation which occurred upon the addition of cupric ions at pH higher than 8 also supports that the complex formation between cupric ion and the free COO^- groups removes the last polar residues in PIA. Furthermore, it was observed that the peak intensities of its ternary complexes were lower and their wavelengths are higher even at pH's between 5 and 7 as those of prepared by using the polymeric ligands based on acrylamide, its N-substituted derivative and their copolymers with AA and IA (Table 4).

The color of binary solutions of copper with Ala, PIA, PNIPAAm, and P(NIPAAm-co-IA, 9.8 mol%) changed from colorless to blue when increasing pH from 4 to 8.

with increasing pH →

$^+NH_3\text{-}CH(CH_3)\text{-}COOH \leftrightarrow {}^+NH_3\text{-}CH(CH_3)\text{-}COO^- \leftrightarrow NH_2\text{-}CH(CH_3)\text{-}COO^-$

(cation) (zwitterion) (anion)

$pK_1 = 2.34$ $pI = 6.00$ $pK_2 = 9.69$

Sch. 3. Ionization equilibria of α-COOH and α-NH_2 groups in Alanine (α-amino acid).

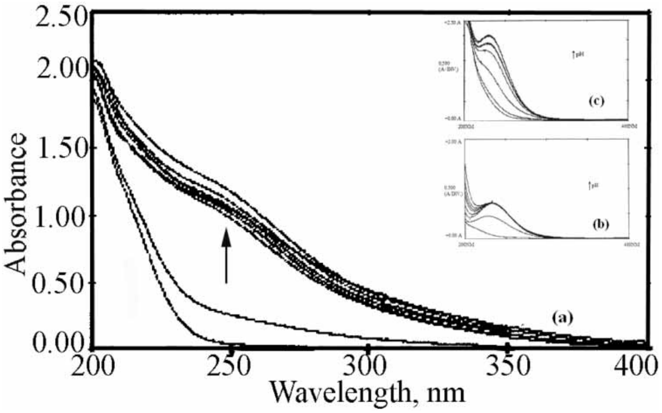


Fig. 7. UV spectra of (a) PAAm-Cu(II) complex diluted 1:2; (b) Ala-Cu(II) complex diluted 1:20; (c) P(NIPAAm-co-IA)-Cu(II) complex diluted 1:7 and at r = 4 in water and in the region of pH = 3–10.

Turbidity of the copper solutions increased with increasing pH from 4 to 8 because of its hydrolysis in aqueous solution. The solutions of all binary complexes except Ala-Cu(II) were light blue, but slightly turbid, while the color of homogeneous solution of Alanine with Cu(II) ions at pH 8 was dark blue. In the case of their ternary complexes, turbidity disappeared and their colors changed to dark blue.

It can be concluded from these results that the presence of amide groups in side chains leads to an increase in the ability to form chelate complexes with amino acid molecules by decreasing the number of dimerized carboxylic acid groups due to strong intramolecular hydrogen bonding, and therefore PAAm, PNIPAAm and their copolymers with AA and IA may form ternary chelate structures, whereas PIA can form mainly carboxylate complexes in the cases of both PIA-Cu(II) and PIA-Cu(II)-Ala complexes. In other words, the lower maximum absorption intensities as to the other samples, even at pH 5 and 6, indicate the presence of highly hydrogen bonded repeating units, resulting from the second carboxyl group.

In addition, the changes in UV spectra of polymer-Cu(II) solutions in the range of 200–400 nm were compared to gain further information about complex formation. The absorption spectra of the polymer- and Ala-Cu(II) complexes in this region have shown a charge transfer band between 250 and 300 nm and, the intensity of this band increased with increasing pH and the following order (Figures 7a–c): PAAm < P(NIPAAm-co-IA) < P(AAm-co-IA) < P(NIPAAm-co-AA) < Ala.

4 Conclusions

The results of both visible and ultra violet absorption spectra, and cyclic voltammograms showed that, due to dilution of strongly complexing functional groups by using copolymers in which weakly coordinating ligands attached to AAm and NIPAAm, the efficiency of coordination centers on IA and AA in the copolymers is higher than those of the homopolymers. It means that the character of the functional groups and their distribution along the polymer chain affect the complex formation capacities of these polymeric ligands. The experimental results presented above supports the fact that the presence of hydrophobic-bulky isopropyl groups and second carboxyl groups, in the cases of homopolymers of NIPAAm and IA reduce the complexing efficiency of polymeric ligands because of incresing steric effects and dimerization, respectively. Further, the spectrophotometric and electrometric results obtained in the range of 200–1100 nm and (−0.800 V)–(+0.600 V), respectively, suggest binary and ternary complex formations in the cases of AA and IA containing copolymers.

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