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Reaction of the acrylic acid and 1-vinylimidazole copolymer with $CuCl_2$ in aqueous solution

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The reaction of acrylic acid—1-vinylimidazole copolymer with $CuCl_2$ in an aqueous medium was investigated by potentiometric titration and UV and ESR spectroscopy. The complex formation involves both the azole units and the carboxy groups. The Cl^- ions are also incorporated in the inner sphere of the complexes, their removal by dialysis resulting in an increase in the coordination capacity of the carboxylate groups.

Key words: copolymer, acrylic acid, 1-vinylimidazole, copper, chloride, complex

The complexes of functionally substituted polymers with transition metal ions have long attracted the attention of researchers,[1,2] not only due to their practical value but also as convenient models of biological macromolecules and enzymes. However, the relationship between the conformations and complex-forming properties of a polymer molecule, the effect of the nature and state of the side functional groups on these properties, or the distribution of metal ions in the bulk of polymer coils have not been adequately studied. In this respect, copolymers of acrylic acid (AA) and 1-vinylimidazole (VI), containing weakly basic imidazole units and carboxy groups, are of considerable interest.

The purpose of this work was to study the complexes of the AA—VI copolymer with copper(II) ions and to elucidate the influence of the ionization of carboxy groups on the structure and coordinate capacity of copolymer macromolecules.

Experimental

The AA—VI copolymer was prepared under conditions of free-radical initiation in the presence of 2,2-azobis(isobutyronitrile) (0.5% of the monomer weight) in boiling acetone (b.p. 56°C) with stirring for 10 h. The AA : VI molar ratio was 4 : 1. The resulting copolymers were purified from unreacted monomers by repeated washing with acetone and ether and dried *in vacuo* to a constant weight. The yield of the copolymer was 20%. According to the elemental analysis for nitrogen, it contained 72.0 mol.% AA (found: N, 5.01 %). Reagent grade copper(II) chloride was additionally recrystallized from water.

The potentiometric measurements were performed on an EV-74 ionometer in a temperature-controlled cell at 25 °C. The initial copolymer was dissolved in water to which a 0.1 *M* solution of alkali was added (15—20% excess relative to the concentration of AA units). The copolymer concentration was 0.01 unit-mole L^{-1} relative to the AA units. A 0.1 *M* solution of HCl was used for titration. The viscosity measurements were conducted by a capillary Ubbelohde viscosimeter at 25 °C.

In investigating the complexes by the equilibrium dialysis method, the solution under study was placed in a dialyzer with a Millipore PVBC membrane (retaining polymers with molecular masses above 3000) and brought into equilibrium with an equal volume of water over a period of 24 h. The concentration of copper ions in the dialyzate was determined by the atomic absorption method on an AAS-1 Karl Zeiss (Jena) spectrometer in the propane—air flame. The amount of metal bound in the complexes was calculated using the formula

$$A = \{([Cu^{II}]_0 - 2\,[Cu^{II}]_d)/[Cu^{II}]_0\} \cdot 100\%,$$

where A is the degree of binding in the complex, %; $[Cu^{II}]_0$ and $[Cu^{II}]_d$ are the concentrations of the Cu^{II} ions in the initial solution and in the dialyzate, respectively.

The UV/Vis absorption spectra of aqueous solutions of the copolymer and its complexes were recorded on a Specord UV-VIS spectrophotometer. The ESR spectra were run on a PS-100X instrument at 25 °C. Diphenylpicrylhydrazine (DPPH) and Mn^{2+} in MgO were used as the field standards. Samples for ESR spectroscopy were prepared by lyophilization of the correspondent solutions.

Results and Discussion

The AA—VI copolymer contains acidic carboxy groups and azole rings capable of exhibiting weak basic properties and of forming hydrogen bonds with electron-deficient hydrogen atoms.[3] Due to the presence of intramolecular hydrogen and ionic bonds, the copolymer is insoluble in water. As the solution pH increases, these bonds are partially cleaved; the appearance of

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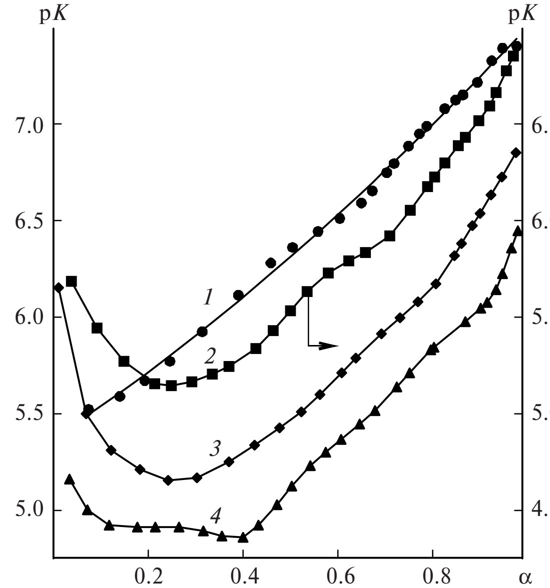


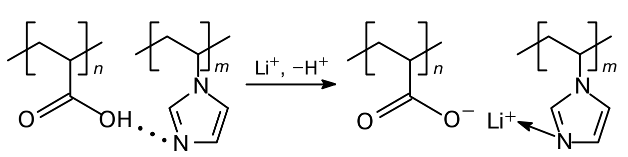
Fig. 1. Potentiometric titration curves of PAA (*1*) and the AA—VI copolymer (*2—4*). Neutralization was carried out with NaOH (*1*, *3*), KOH (*2*), and LiOH (*4*); [PAA] = [AA—VI] = 0.006 mol L^{-1} (relative to the acidic groups); α is the degree of ionization.

negative charge on the polymer chain promotes uncoiling of macromolecules and dissolution of the copolymer. In the case of incomplete neutralization of acidic groups, these groups can react with the VI units in the solution, which is expected to affect the acidic properties of the copolymers.

Indeed, the curve of titration of the AA—VI copolymer with NaOH plotted in the p*K*—α coordinates (α is the degree of ionization) is located below the titration curve of pure polyacrylic acid (PAA) (Fig. 1). Apparently, this is related to the partial suppression of the electrostatic effect upon ionization of the AA units separated by the VI units. The known copolymerization constants of these monomers (r_{VI} = 0.02, r_{AA} = 0.24)[4] suggest that the copolymer consists of single VI units and short (2 or three 3 units) blocks of AA. For both copolymers, sections of decreasing p*K* following an increase in the degree of ionization are typically observed. The increase in the acidity in this region seems to be caused by the destruction of intramolecular hydrogen and ionic bonds between the AA and VI units.

The curves of titration with the KOH and LiOH bases follow the same pattern (see Fig. 1). In the latter case, a slight shift of the curve toward lower p*K* values was observed; this is in line with the more pronounced trend of Li^+ ions to accumulate on the polyacid chains. In addition, it can be suggested that the protons in the hydrogen (ionic) bonds between the AA and VI units are replaced by the Li^+ ions. This should also enhance the copolymer acidity (Scheme 1).

Scheme 1



It is known[1] that reactions of polymeric acids with transition metal salts are accompanied by a decrease in the pH due to the reactions

$$M^{n+} + HA \rightleftharpoons MA^{(n-1)+} + H^+,$$

$$M^{n+} + A^- \rightleftharpoons MA^{(n-1)+}.$$

Thus, potentiometric measurements can be used to monitor this reaction. Indeed, the pH of a copolymer solution decreases as a solution of $CuCl_2$ is added to it (Fig. 2); sections characterizing the formation of complexes with different compositions can be distinguished in curves *2* and *3*, plotted for degrees of neutralization (β) of 0.6 and 1, respectively. The region of copolymer saturation with the Cu^{II} ions shifts to higher copper concentrations as the degree of copolymer neutralization increases.

In the quantitative analysis of the reactions of polymeric acids with transition metal ions, the Bjerrum method[5] is used to calculate the formation constants

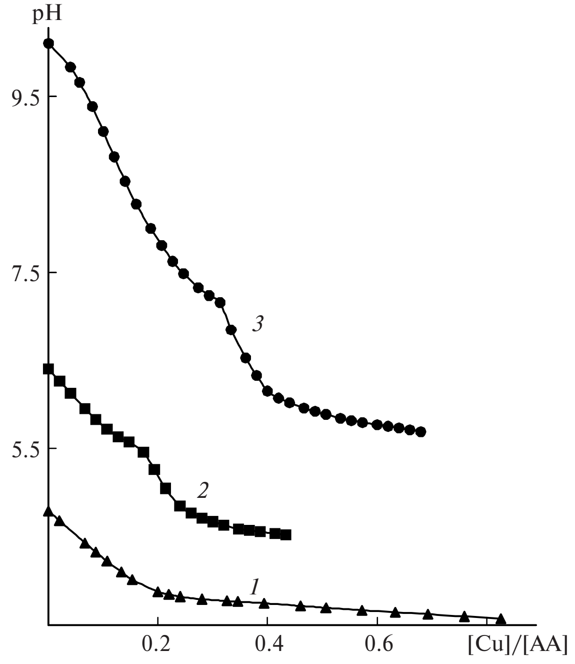


Fig. 2. Curves of potentiometric titration of the AA—VI copolymer with a solution of $CuCl_2$. The degree of polymer neutralization: 0.2 (*1*), 0.6 (*2*), 1.0 (*3*). [AA—VI] = 0.0075 mol L^{-1} (relative to the acidic groups); [$CuCl_2$] = 0.1 mol L^{-1}.

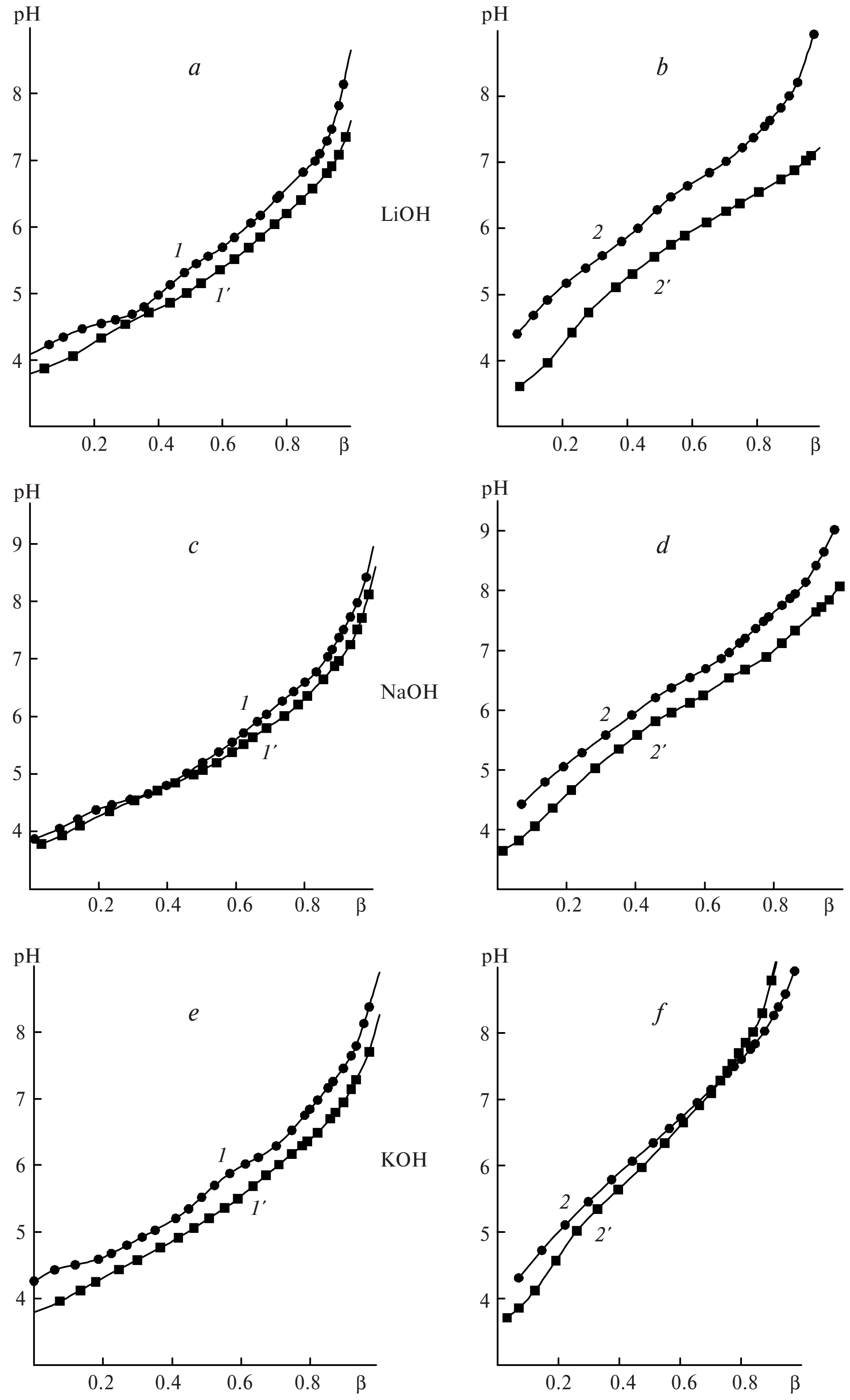


Fig. 3. Titration curves of the AA—VI copolymer (*1*), PAA (*2*), and their complexes with Cu^{II} (*1′*, *2′*). Neutralization was carried out with LiOH (*a*, *b*), NaOH (*c*, *d*), and KOH (*e, f*). [AA—VI] = [PAA] = 0.01 mol L^{-1} (relative to the acidic groups); $[CuCl_2]$ = 0.0005 mol L^{-1}; β is the degree of neutralization of the carboxy groups.

and coordination numbers. This method implies comparison of potentiometric titration curves for the polymer and its complex. This approach is based on the assumption that the nonbonded carboxy groups in the free polymer and in the complex have the same acidity. This assumption is valid only when complexation exerts no significant influence on the conformations of noncomplexes segments of the polymer molecule. The AA—VI copolymers, which involve substantial intramolecular interactions, are expected to undergo strong conformational changes upon the interactions with $\mathrm{Cu^{II}}$ ions.

Actually, the curves for potentiometric titration of the polymers and complexes are substantially different for PAA and the AA—VI copolymer (Fig. 3). In the case of PAA, the pH value of the solution of the complex decreases over the whole range of the degrees of neutralization β of the carboxy groups, whereas in the case of the copolymer, curves for neutralization of the carboxy groups with alkalis (LiOH ore NaOH) tend to undergo a smaller shift in the presence of copper(II) ions; the titration curves approach each other when $\beta \approx 0.4$. This can be due to the lower stability of copolymer complexes. Hence, they were studied by the equilibrium dialysis method. The results obtained reflect the substantially higher stability of the complexes formed by the AA–VI copolymer (Fig. 4). In the PAA-containing system, the high (>90%) degree of binding of $\mathrm{Cu^{II}}$ ions is observed only for high β values, the complex being partially destroyed in a more acid regions. In the presence of the copolymer, the complex does not virtually dissociate at either low or high degrees of neutralization but it partially decomposes when $\beta \approx 0.6$ during neutralization by alkali (LiOH or NaOH).

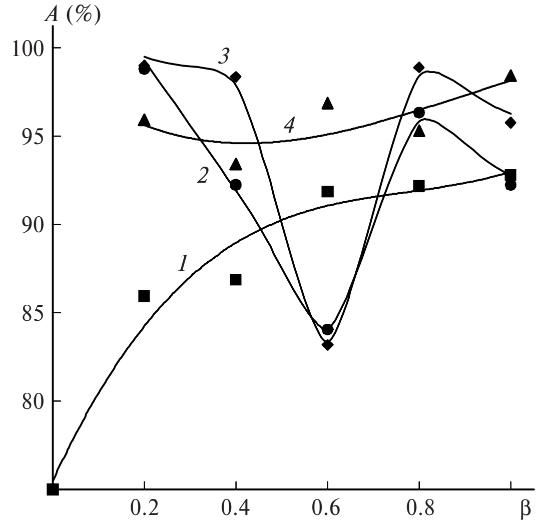


Fig. 4. Degree of binding (*A*) of $\mathrm{Cu^{II}}$ into the complex with PAA (*1*) and the AA—VI copolymer (*2—4*) *vs.* degree of neutralization (β) of the carboxy groups. Neutralization was carried out with NaOH (*1*, *3*), LiOH (*2*), and KOH (*4*); [PAA] = [AA—VI] = 0.01 mol $\mathrm{L^{-1}}$ (relative to the acidic groups).

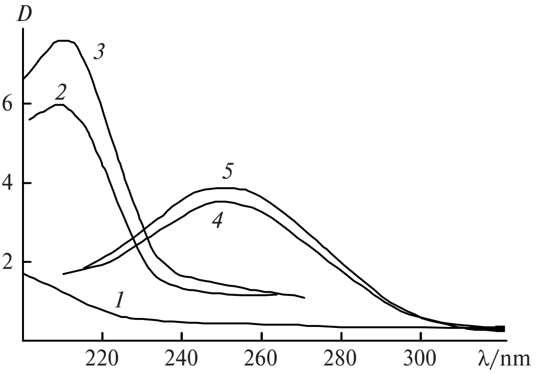


Fig. 5. UV spectra of PAA (*1*), PVI (*2*), PVI—$\mathrm{Cu^{II}}$ (10 : 1, *3*), and PAA—$\mathrm{Cu^{II}}$ (10 : 1) for degrees of neutralization (β) of the carboxy groups of 0.8 (*4*) and 1 (*5*). [PVI] = [PAA] = 0.01 mol $\mathrm{L^{-1}}$. The cell thickness is 1 mm. Under these conditions, a 0.01 *M* solution of $\mathrm{CuCl_2}$ is transparent.

The enhanced stability of the copolymer complexes at low β values and the less pronounced decrease in the pH upon complex formation compared to that for PAA complexes can be due to the preferential complexation with the imidazole units. To specify the coordination centers in the AA—VI copolymers, spectroscopic studies in the UV and visible regions and ESR studies were carried out.

The introduction of copper(II) into solutions of PAA and poly-1-vinylimidazole (PVI) induces changes in the UV spectra (Fig. 5). A new band at 250 nm corresponding to the formation of the complex appears in the PAA spectrum, whereas in the PVI spectrum, the intensity of the absorption band at 209 nm slightly increases. The addition of $\mathrm{Cu^{II}}$ ions to the AA—VI copolymer does not change the spectral pattern in the region of absorption of the azole units (Fig. 6); however, it induces the appearance of a band at 250—270 nm, which can be attributed to the complex of copper(II) with carboxylate groups.

The solutions of the copolymer studied and the corresponding homopolymers are optically transparent

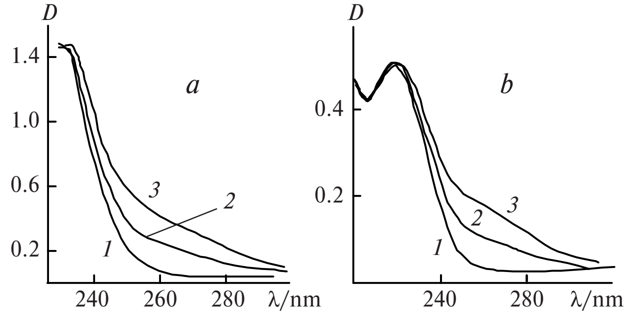


Fig. 6. UV spectra of the AA—VI copolymer (*1*) and its complex with $\mathrm{CuCl_2}$ (*2*, *3*) for degrees of neutralization (β) of the carboxy groups in the AA units equal to 0.8 (*a*) and 1 (*b*). [AA—VI] = 0.01 mol $\mathrm{L^{-1}}$ (relative to the acidic groups), the AA (units) : $\mathrm{Cu^{II}}$ ratio is 10 : 1 (*2*) and 5 : 1 (*3*). The cell thickness is 0.2 mm.

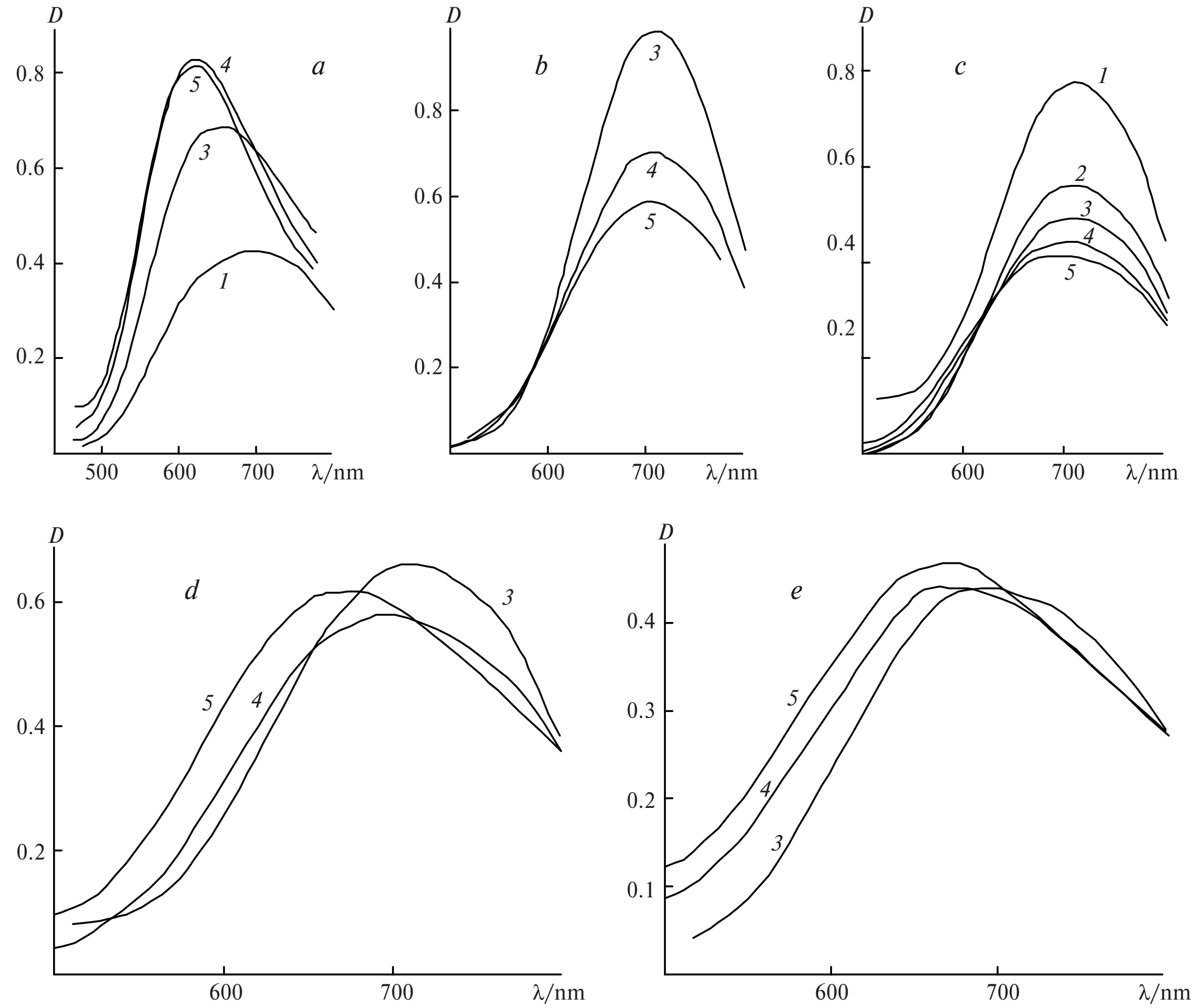


Fig. 7. Absorption spectra of Cu^{II} complexes with PVI (*a*), PAA (*b*, *c*), and the AA—VI copolymer (*d*, *e*). The degree of neutralization (β) of the AA units is 0.8 (*b*, *d*) or 1 (*c*, *e*). [PVI] = [PAA] = [AA—VI] = 0.00625 (*1*), 0.01 (*2*), 0.0125 (*3*), 0.025 (*4*), 0.05 mol L^{-1} (*5*) (relative to polymer units); [$CuCl_2$] = 0.0025 mol L^{-1}. The cell thickness is 50 mm.

in the visible region but their complexes with copper(II) exhibit characteristic absorption in this region (Fig. 7). As the [PVI] concentration increases, the absorption band shifts from 695 nm to 620 nm and its intensity increases, which is consistent with the results of previous works.[6,7] The PAA complexes show absorption in the 710—715 nm range, which decreases upon an increase in the PAA : [Cu^{2+}] ratio with the copper(II) concentration remaining constant. The unusual concentration dependence observed may be due to the cooperative type of copper(II) interaction with polymers;[1] this is especially pronounced for high degrees of neutralization of the carboxy groups (β) when electrostatic expansion of the polymer chain prevents the formation of complexes with a high degree of metal coordination. The increase in the relative content of Cu^{II} up to a particular limit results in a higher degree of coordination due to compensation of the negative charge of the chain and in a smaller loss in entropy upon the interaction of metal ions with the sections of macromolecules that have already been partially cross-linked. The formation of bi- and polynuclear complexes exhibiting more intense absorption in the visible region[8] becomes possible.

The intensity of absorption of copolymer complexes virtually does not depend on copolymer concentration but the absorption band shifts from 675 nm to 710 nm as the concentration decreases. Further decrease in the concentration of the copolymer results in its sedimentation. Thus, with excess AA units in the copolymer (20 : 1), both the AA and VI units participate in the complexation. A decrease in the copolymer content in the complex shifts the equilibrium toward the carboxylate complex; this is in line with the above-noted behavior of the PAA—Cu^{2+} complexes. We were unable to investigate the behavior of the complexes with medium and low β values because lower degrees of neutralization in combination with relatively high concentrations, which

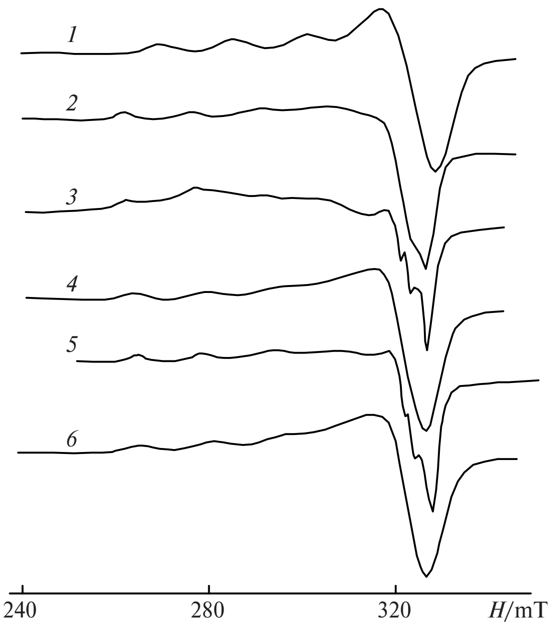


Fig. 8. ESR spectra of Cu^{II} complexes with PVI (*1*), PAA (*2*, *3*) and the AA—VI copolymer (*4*—*6*). The degree of neutralization (β) of the AA units is 0.2 (*2*, *4*) and 1 (*3*, *5*, *6*). Neutralization was carried out with NaOH (*2*—*5*) and LiOH (*6*).

are normally used in spectrophotometry, resulted in turbidization of the solutions.

The copper(II) complexes with the AA—VI copolymer exhibit ESR spectral patterns typical of copper(II) tetragonal complexes with a rather well-resolved HFS in the parallel orientation and, in some cases, also in the perpendicular orientation (Fig. 8). When considering the spectral parameters (Table 1), three groups of complexes can be distinguished. The parameters of the first group ($A_\parallel \approx 14.1$ mT; $g_\parallel = 2.335$—2.345) coincide with those for the complex with PAA. The parallel HFS component is well-resolved in these spectra, the HFS lines in the perpendicular region being fairly narrow (2—3 mT). Thus, it can be suggested that copper(II) atoms in these complexes are distributed fairly uniformly along the polymer chain. Among complexes of carboxy polymers with Cu^{II}, structures in which one to four carboxy groups are coordinated to a copper(II) atom have been described.[9,10] In the case of systems under consideration, coordination to two carboxylate groups is probable because a higher degree of coordination would require a substantial compaction of the polymer coil. This results in broadening of the spectral lines. The parameters of the given spectra differ from analogous data for the PAA complexes with copper(II) nitrate ($A_\parallel = 12.3$ mT, $g_\parallel = 2.343$);[11] this is probably due to the retention of the Cl$^-$ ions in the inner sphere of the complex caused by the fact that they are coordinated to Cu^{II} ions more strongly than NO$_3^-$ ions. Because of the reduced coordination capacity, copper chloride is distributed more evenly in the polymer bulk.

Table 1. Parameters of the ESR spectra of PAA and AA—VI copolymer complexes with Cu^{2+} ions

Ligand, copolymer	β	$A_\parallel \cdot 10^{-4}$	$A_\perp \cdot 10^{-4}$	$g_\parallel$	$g_\perp$
		mT			
PVI	—	16.1	—	2.271	2.025
PAA^a	1.0	14.1	2.0	2.335	2.060
	0.8	14.1	2.0	2.335	2.060
	0.6	14.1	2.0	2.335	2.061
	0.4	14.1	2.0	2.335	2.060
	0.2	14.1	—	2.340	2.035
	0	13.2	—	2.325	2.040
AA—VI^b	1.0	16.1	—	2.276	2.022
AA—VI^a	1.0	14.1	—	2.333	2.048
	0.8	14.1	—	2.333	2.048
	0.6	14.1	—	2.333	2.048
	0.4	14.1	—	2.332	2.050
	0	14.1	—	2.333	2.046
AA—VI^c	1.0	14.1	2.3	2.337	2.056
	0.8	14.1	2.4	2.339	2.058
	0.6	14.1	—	2.339	2.060
	0.4	14.1	—	2.339	2.037
	0	16.1	—	2.306	2.042
AA—VI^d	1.0	14.1	2.0	2.334	2.061
	0.8	14.1	2.0	2.334	2.060
	0.6	14.1	2.0	2.334	2.060
	0.4	16.1	—	2.295	2.034
AA—VI^e	1.0	16.0	—	2.304	2.045
AA—VI^f	1.0	15.3	—	2.297	2.036
	0.8	15.3	—	2.299	2.036
	0.6	15.3	—	2.299	2.036
	0.4	15.3	—	2.306	2.038
	0.2	15.3	—	2.306	2.036

Note. The [polymer units] : [Cu^{2+}] ratio is 20 : 1.
Preparation conditions:
[a] NaOH;
[b] NaOH, ligand : Cu^{2+} = 100 : 1;
[c] NaOH, dialysis;
[d] KOH;
[e] LiOH;
[f] LiOH, dialysis.

The second group of complexes is similar to the Cu^{II} complex with PVI in ESR spectral parameters ($A_\parallel = 16.1$ mT; $g_\parallel = 2.271$); the HFS in the perpendicular area is not resolved in the spectra of these complexes. Previously,[12] a study of the PVI—CuSO$_4$ system for a copper ion coordinated to four azole units gave the $A_\parallel = 16.9$ mT value, which differs somewhat from the value found in the present work. This may also be related to a decrease in the number of azole ligands in the copper(II) complex caused by the fact that it contains also Cl$^-$ ions. Copolymer complexes of this type are formed when the degree of neutralization is low, a substantial excess of the copolymer is used, and LiOH is employed to neutralize the COOH groups. In all of these cases, the capacity of carboxylate units for coordination is reduced due to the protonation at low degrees of neutralization β, electrostatic effects at high β, and binding of Li$^+$ ions to the carboxylate anions.

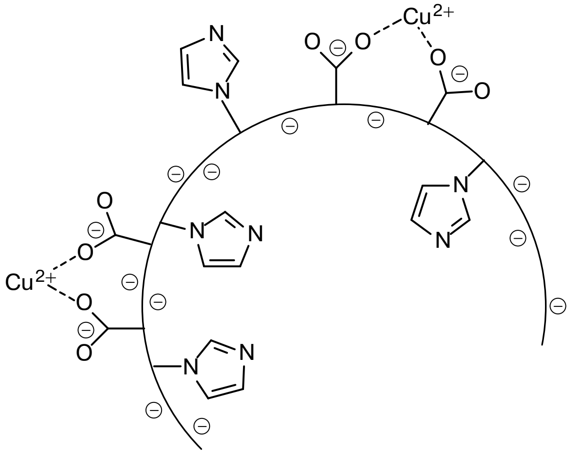
The partial removal of Li^+ cations during dialysis induces the formation of complexes whose parameters do not change over a broad range of β values and are intermediate between those of the spectra considered above. The width of the HFS lines is greater than the HFC constant; thus, the HFS lines are not resolved in the "perpendicular" region, which is typical of relatively compact complexes. Apparently, in this case, a mixed copper(II) complex incorporating both carboxylate groups and imidazole units is formed.

The data obtained point to preferential coordination of Cu^{II} to the AA groups, while the imidazole units take part in the reaction only when the capacity of carboxylate groups for coordination to copper(II) ions is deteriorated.

The results obtained here permit the following conclusions concerning the interactions in the copolymer—Cu^{II} system.

1. At high degrees of neutralization, the AA—VI macromolecules occur in the uncoiled conformation, their complexation with copper(II) being similar to that observed for PAA. The inner sphere of the complex includes one or two adjacent AA units, while the VI units react only when the coordination capacity of the carboxylate groups has been deteriorated due to either strong electrostatic expansion of the polymer chain or the interaction with alkali metal ions (Scheme 2).

Scheme 2



2. The decrease in the degree of neutralization is accompanied by a significant compaction of macromolecules of the complex, which is more pronounced in the case of the copolymer than in the case of PAA, as indicated by viscosity measurements (Fig. 9). Apparently, the interaction with copper(II) ions is favorable for the involvent of other association mechanisms, *i.e.*, association by means of hydrogen and ionic bonds and coordination involving alkali metal ions (Scheme 3).

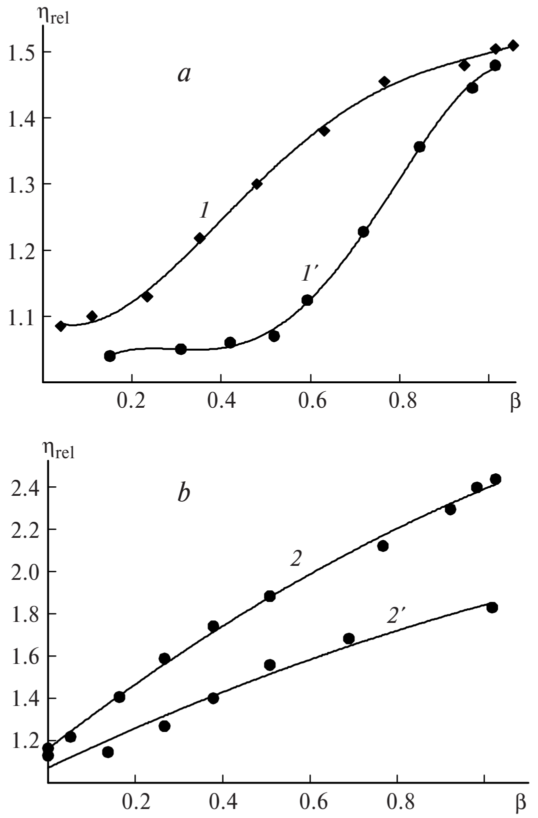
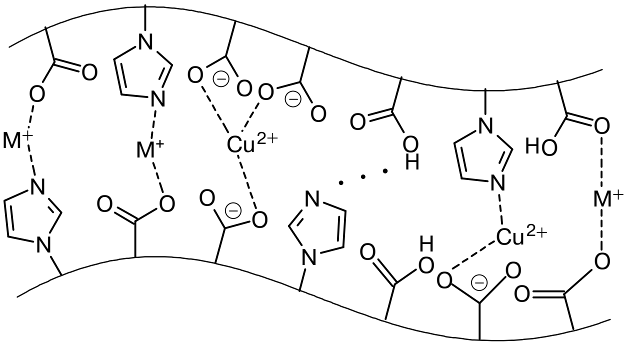


Fig. 9. Relative viscosity of solutions of the AA—VI copolymer (*1*), PAA (*2*), and their complexes with Cu^{II} (*1'*, *2'*) *vs.* the neutralization degree (β) of the carboxy groups. [AA—VI] = [PAA] = 0.01 mol L^{-1} (relative to the acidic units); $[CuCl_2]$ = 0.0005 mol L^{-1}.

Scheme 3



Stabilization of hydrogen bonds with participation of the COOH groups decreases the acidity of these groups and counterbalances, to some extent, the decrease in the pH upon complexation; as a consequence, traditional potentiometric methods are inapplicable to systems of this type.[5] Despite the synergistic character of these interactions, the Cu^{2+} and Na^+ or Li^+ ions compete for binding to the polymer chain, which results in loosening of copper(II) coordination in the region of $\beta = 0.6$ where the compaction of the macromolecule of the complex becomes close to its limit but the content of the alkali metal carboxylates is fairly high. The absence of this effect in the case of K^+ ions is explained by their lower coordination capacity.

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