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New amphoteric chelating/ion exchange resins with substituted carbamylethylenephosphonates; synthesis and EPR studies of their Cu(II) complexes

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Abstract

Two new chelating/ion-exchange resins have been obtained by amination of vinylbenzyl chloride–styrene–divinylbenzene copolymer, bearing ethoxycarbonylethyl phosphonate, with ethylenediamine and diethylenetriamine. The effect of close proximity of acidic and basic sites of ligand on chelating/ion-exchange of four divalent metal cations has been studied. In order to explain the behavior of the synthesized resins, a series of reference resins has been obtained. These resins have same types of functional groups—phosphonic acid and *N*-substituted amide of carboxylic acid but deposited randomly within polymer material. It has been found that close proximity of both acidic and basic sites, interacting with each other, gave antagonistic effect at pH 3.7 and 5.6 and suppressed uptake of Cu(II), Cd(II), Ni(II) and Zn(II) from weakly acidic solutions. For example Resins 1 and 2 with carbamylethylenephosphonates displayed at pH 3.7 log K_d Cu(II) 2.10 and 3.06, whereas reference Resins 3 and 4 had log K_d Cu(II) 2.83 and 4.50, respectively. EPR studies of Cu(II) complexes formed in each case were used to explain the observed effect. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical modification; Chelating resins; EPR studies

1. Introduction

Insoluble polymers bearing immobilized low-molecular complexing agents are widely used for the removal of metal cations from aqueous solutions. This ability is utilized in the preconcentration of cations before their analysis is possible, in purification of water and treatment of wastewater, as well as in several applications in hydrometallurgical processes. Among these materials are also ones with immobilized amines, as they are well-known complexones for many transition metal cations. Examples of such polymers include oligoethyleneimines [1–4], triazole [5] and pyrazole [6] compounds immobilized on polymer matrices. These complexing resins, being weakly basic, are at the same time sensitive towards changes of pH. At low pH, competition from protons is strong and therefore such resins are not suitable for ion removal under acidic condition.

Another class of ion-exchange/complexing resins is formed by those containing phosphonate groups—medium strength acid. Examples include phosphonate resins used for removal of uranium from seawater [7] and resins with various phosphorus containing ligands [8]. Also, phosphonic acid resins containing another group in the geminal position were described lately. This second group can be the same (giving methylenediphosphonate polymers) as that published in Refs. [9,10], or different, resulting in ethylenediphosphonate and carboxyethylphosphonate resins [11,12]. The presence of the second group influences complexes' properties of the resin as described in Refs. [9,11], changing the acidity of the ligand, its net charge at a given pH, hydrophilicity and the type of complexes which can be formed with cations. Since carboxyethylphosphonate ligands presented previously [11] have an ester of carboxylic acid present and offer a possibility of selective modification, in this paper we would like to extend the studies of the effect of the second group on resin ion uptake by introducing nitrogen donors to the structure of the ligand. Chemical modification of carboxyethylphosphonate resins can be performed using diamines, and obtained resins would possess ligands, which are similar in nature to well-known low-molecular complexing agents—carbamylalkylenephosphonates.

The aim of this work is to synthesize new chelating

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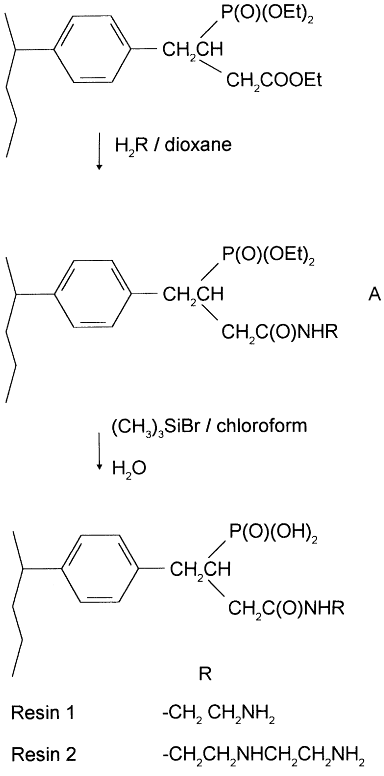

Fig. 1. Scheme of investigated resins' synthesis.

resins, starting from polymer-bearing carboxyethylphosphonate, by their modification with ethylenediamine and diethylenetriamine, thus leading to carbamylethylenephosphonates, and to investigate their complexing properties.

2. Experimental

2.1. Materials

Copolymer of vinylbenzyl chloride (VBC), styrene (St) and technical divinylbenzene (DVB) having 2 wt.% degree of crosslinking is prepared as described in Ref. [11]. This polymer is reacted with diethyl ethoxycarbonylethyl phosphonate obtained as described in Ref. [12] using a previously published procedure [11]. The resins investigated in this study are obtained by reacting VBC/St/DVB copolymer bearing diethyl ethoxycarbonylethylphosphonate groups with diamines. Thus, Resin 1 is obtained by reacting 3 g of the aforementioned copolymer with 20 ml of ethylenediamine and refluxing the mixture for 17 h. The product obtained is washed with water, 1 M HCl, water, 1 M NaOH, water, acetone and dried. It is subsequently hydrolyzed using 16 mmol of sodium bromide, 10 g of trimethylchlorosilane and 10 g of dry acetonitrile for each gram of polymer. Reaction is carried out for 4 h under reflux. In a second step, the polymer is separated, hydrolyzed using water and conditioned using 1 M HCl and 1 M NaOH solutions. Resin 2 is obtained in a similar manner with diethylenetriamine; temperature of the reaction is 130°C.

Reference Resins 3 and 4, both having phosphonate and amino functionalities on separate units, are synthesized using a multistep procedure. First, VBC/St/DVB copolymer is reacted with excess of triethyl phosphite/dioxane 1:1 v/v mixture under reflux for 16 h. Under such conditions only a part of chloromethyl groups react, leaving some still available for subsequent modification with potassium cyanide. This reaction is carried out using 9 g of partially phosphonated polymer, 3 g of KCN in 80 ml of dimethylformamide refluxing mixture at 80°C for 4 h. This intermediate is subsequently subjected to aminolysis with ethylenediamine (Resin 3) and diethylenetriamine (Resin 4) followed by hydrolysis of phosphonate ester with $(CH_3)_3SiCl/NaBr$ in acetonitrile as in the case of Resins 1 and 2.

Reference Resin 5 with phosphonate groups is obtained by simple Arbusov reaction on VBC/St/DVB polymer as described elsewhere [13]. Reference Resins 6 and 7, with amino groups only, are obtained by a two-step procedure—first reacting VBC/St/DVB copolymer with potassium cyanide and subsequently with respective amines. Reaction conditions are the same as for Resins 3 and 4.

2.2. Methods

In order to determine sorption capacity of resins towards Cu(II), Cd(II), Ni(II) and Zn(II), they are reacted with 10^{-4} N M(II) solutions (M = Cu(II), Cd(II), Ni(II) and Zn(II)) in 0.2 M acetate buffer at a pH of 3.7 and 5.6. Thus, enough resin to give 0.05 mmol of ligand (equivalent of 0.10 mmol of nitrogen in Resins 1, 3 and 6 and 0.15 mmol of nitrogen in Resins 2, 4 and 7) is shaken with 10 ml of the given metal solution for 24 h. Then the solution is filtered and the metal ion concentration is measured using atomic absorption spectroscopy on Perkin–Elmer Aanalyst 100 spectrophotometer with wavelength set at 324.8, 228.8, 232.0 and 213.9 nm for Cu(II), Cd(II), Ni(II) and Zn(II), respectively.

The nitrogen content is measured using the Kjeldahl method digesting approximately 0.5 g of resin in 25 ml of concentrated sulfuric acid.

The phosphorus content is measured by digesting approximately 20 mg of resin in 15 ml of perchloric acid followed by spectrophotometrical determination of complex with amidol at 700 nm.

The EPR spectra were recorded on a Bruker ESP 300 E spectrometer operating at X-band (9.1–9.9 GHz) and equipped with the Bruker NMR gaussmeter ER 035 M and the Hewlett–Packard microwave frequency counter. The spectra were analyzed by computer simulation program based on resonance fields calculated according to method of Sakaguchi et al. [14]. The EPR experiments were performed at 77 K and at room temperature on resins swollen in 10 ml of 1×10^{-4} M $Cu(NO_3)_2$, separated by filtration and air dried. Spectra were recorded after 2 days of pH adjustment

Table 1
Characteristics of obtained resins

Resin	Phosphorus content (mmol/g)	Nitrogen content (mmol/g)	Percentage of solid (%)	Water regain (g/g)
1	1.85	3.90	47.17	1.12
2	1.66	5.27	37.88	1.64
3	1.82	3.14	47.62	1.11
4	1.60	4.42	36.63	1.73
5	3.65	0.00	40.48	1.47
6	0.00	5.92	56.50	0.77
7	0.00	9.36	47.62	1.10

of the resin with either HCl or NaOH at constant ionic strength ($I = 0.5$ M).

3. Results and discussion

3.1. Synthesis of resins

The VBC/St/DVB polymer with 2 wt.% of crosslinking agent has been subjected to reaction with sodium derivative of diethylethoxycarbonylethyl phosphonate as described earlier [11]. This reaction resulted in polymer with phosphorus content of 2.15 mmol/g. Residual Cl concentration was measured as well, giving less than 0.1 mmol/g. Low Cl content is essential for the planned route of modification because it allows for further chemical reactions on polymer without introducing unwanted ligands into the structure of resins (like in the case of side reaction of amine with chloromethyl groups). The above polymer has been subjected to amination with ethylenediamine and diethylenetriamine (see Fig. 1). In the case of ethylenediamine intermediate, product A had phosphorus content of 1.81 mmol/g, nitrogen content of 3.77 mmol/g and water regain of 1.63 g/g. For diethylenetriamine the values are 1.54, 5.07 and 1.68 g/g, respectively. These values fit well, within experimental error, into what would be expected—in the case of ethylenediamine nitrogen content is twice and in the case of diethylenetriamine three times higher than the phosphorus content. Both polymers have been subsequently subjected to reaction with trimethylchlorosilane/sodium bromide in acetonitrile, converting their phosphonate groups to trichloromethylsilyl esters, which are very sensitive towards hydrolysis [15]. After washing with water and conditioning, Resins 1 and 2 have been obtained and their properties are given in Table 1.

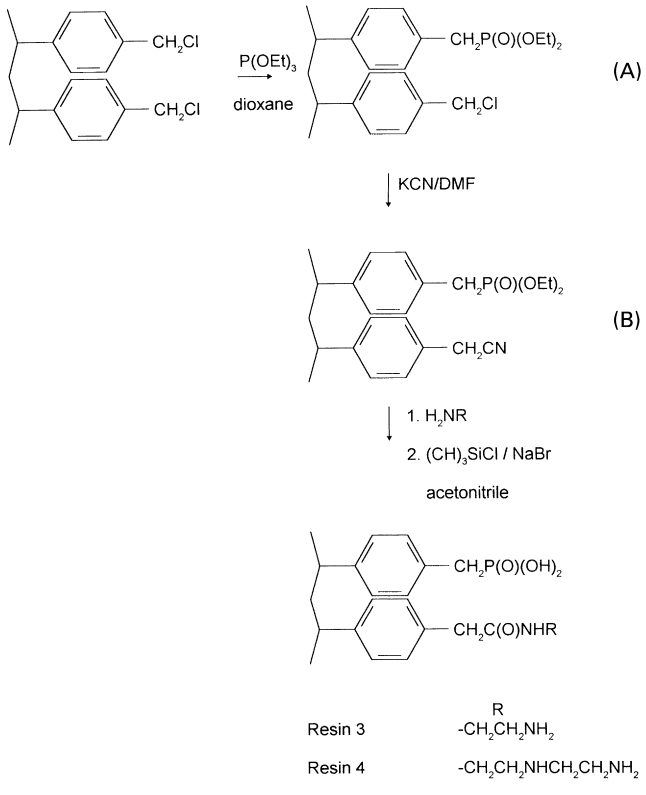

Fig. 2. Scheme of reference resins' synthesis.

In order to prepare the reference resins, which would contain the same functionality as Resins 1 and 2, but deposited randomly in polymer, a synthetic route depicted in Fig. 2 has been chosen. First it was necessary to only partially functionalize the VBC/St/DVB copolymer, so that some chloromethyl groups would be left unchanged for subsequent modification. This has been achieved by refluxing polymer with 1:1 v/v mixture of dioxane and triethyl phosphite. This leads to an intermediate A in Fig. 2 with a phosphorus content of 1.85 mmol/g and Cl content of 1.49 mmol/g. This obtained polymer intermediate has been subsequently reacted with potassium cyanide as described in Ref. [16], resulting in polymer B with a phosphorus content of 1.90 mmol/g and nitrogen content of 1.50 mmol/g. From this point on, the modification has been performed like in the case of Resins 1 and 2, giving finally Resins 3 and 4. Their characteristics are displayed in Table 1. It should be noted here that in both cases it has been possible to achieve ratio of phosphonic groups to amide of carboxylic acid close to 1:1 as in the investigated Resins 1 and 2. For Resin 3, the ratio is 1:1.16 and for Resin 4, 1:1.09. This should allow for a direct comparison of the resins' performance in ion removal from aqueous solutions.

3.2. Metal ion uptake

Metal ion uptake was studied using buffered solutions having a pH of 3.7 and 5.6. Buffered solutions were used in order to keep the resins in one ionic form and to avoid small pH changes that usually take place when weak or medium acidity resin in hydronium form is reacted with slightly acidic or neutral solutions.

From a solution at pH 3.7, only Cu(II) is taken by all investigated resins. It reflects the known affinity of nitrogen-containing ligands towards copper ions as well as preference of phosphonic resins towards these metal ions. The highest value of distribution coefficient is achieved by

Table 2
Uptake of metal ions by investigated resins expressed as logarithms of distribution coefficient (−: Resin does not remove ions under experimental conditions; +: Resin removes all available ions under experimental conditions)

Resin	log K_d							
	Cu(II)		Cd(II)		Ni(II)		Zn(II)	
	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6	pH 3.7	pH 5.6
1	2.10	3.77	1.42	1.99	−	2.00	−	2.75
2	3.06	+	−	1.58	−	2.57	−	2.40
3	2.83	+	2.36	3.11	1.92	2.81	2.54	2.84
4	4.50	+	0.66	1.84	0.66	3.31	−	2.67
5	+	+	4.80	4.46	4.37	3.63	3.83	3.82
6	1.84	2.57	0.93	1.07	1.24	1.26	−	−
7	3.04	4.49	1.29	1.52	1.51	2.51	0.57	1.18

Resin 5, having phosphonic groups only, in which Cu(II) is freely ion-exchanged, and by Resin 4, containing phosphonic groups and diethylenetriamine-substituted amides of carboxylic acid distributed randomly within polymeric matrix (see Table 2). It can be noted that the introduction of amide groups brings down distribution coefficient but it is still some 30 times higher than the value obtained for either Resin 2 or Resin 7. It means that both phosphonic and amide groups of Resin 4 participate in copper complex formation (see Section 3.3) but when they are a part of one group (as in Resin 2) the probability of formation of an zwitterionic structure is greatly enhanced as both of them are in close proximity. Interactions of positively charged amino groups and negatively charged phosphonic groups prevents to some extent the ion exchange of Cu(II) by $-P(O)(OH)O^-$. An increase of pH to 5.6 results in resin being converted into a form in which phosphonic groups are fully dissociated leading to a higher log K_d value. Under the same conditions amino groups are deprotonated, which is reflected by higher uptake of metal ions by Resins 6 and 7.

A similar effect, although to a lesser extent, is observed in the case of resins with 2-aminoethyl substituted amides of carboxylic acid. Resin 6 has log K_d of 1.84, Resin 1 with phosphonic group being close to the amide, has log K_d of 2.10 but again, the highest value has been obtained when both groups are distributed randomly, i.e. for Resin 3. However, in this case, the distribution coefficient is only five times higher than for Resin 1. It can be assumed that a shorter substituent containing only one amino group is not able to reach phosphonic groups and form zwitterions. In other words, in Resin 3 it has been possible to obtain at least partial separation of active groups within the polymeric matrix. This conclusion is supported by the fact that this resin is able to form Cu(II) complexes with O4 donor set much like phosphonic Resin 5 (see Section 3.3).

Other metal ions studied in this work display similar patterns but complex formation is not as efficient as in the case of Cu(II). A probable explanation is that phosphonic resins have weaker affinity towards Zn(II) and in particular towards Ni(II) than for Cu(II) as reported in Ref. [17]. Also various ligands with amino groups are known to be far more effective in the removal of Cu(II) than in the removal of any other divalent metal ion [18]. These two reasons in addition to a possible formation of zwitterionic structures result in poor uptake or no uptake of ions other than Cu(II) at pH 3.7. When pH has been increased to 5.6 uptake of metal ions is significantly improved. As in the previous case (at pH 3.7) here again Resins 3 and 4 with active groups placed separately perform better than Resins 1 and 2 with carbamylethylenephosphonate. Ni(II) and Zn(II) are preferred over Cd(II), a pattern displayed by resins containing amino groups [18]. The only exception is Resin 3, showing log K_d value of 3.11, indicating again that site separation allows for an exchange of Cd(II) by phosphonic groups. Phosphonate resins have higher affinity towards Cd(II) than towards Ni(II) or Zn(II) ions [17].

3.3. EPR and electronic spectra

Analysis of the EPR spectrum of Cu(II)–Resin 3 system, obtained at pH 3.2 at 77 K, shows that its parameters are typical for Cu(II) ions surrounded by monodentate oxygen donors. Furthermore, the value of A_{II} (2.418), higher than usually observed for tetragonal Cu(II)–aqua complex [19], suggesting that phosphonic groups occupy axial positions leaving water molecules bound in Cu(II) plane according to the structure I (Fig. 5). Spectral parameters of the complex I are identical with those observed for complexes formed by Resin 5, containing phosphonic groups only. Immobilization of Cu(II) ions by coordination of the resin phosphonic groups is strongly supported by the fact that anisotropic spectra can be obtained also at room temperature. Fig. 3 shows the EPR spectra in which it is evident that with the increase of pH in the range of 3.0–4.7 intensity of broad line “c”, connected with Cu–aqua complexes of high mobility is getting lower, whereas at the same time intensity of “a” and “b” lines, corresponding to the perpendicular region of the spectra assigned to Cu(II) complexes I and II, respectively, is growing. First line of copper hyperfine structure (of parallel orientation), “a′”, is seen in all spectra recorded

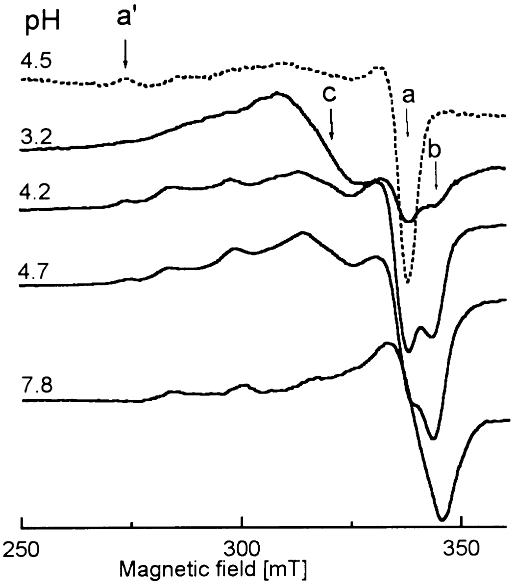

Fig. 3. EPR spectra of the copper (II)–Resin 5 (dotted line) and copper (II)–Resin 3 (solid lines) systems as a function of pH at room temperature.

up to the pH of 6.5 at 77 K. This means that complex with O4 donor set is relatively stable and within pH range 3.8–6.5 exists in equilibrium with two other complexes—II and IIa (Fig. 4a). N2O2 donor set for Resin 3–Cu(II) complex is postulated on the basis of significant increase of A_{II} and decreases of g_{II} values, which is characteristic for complexes in which amino groups are involved in Cu(II) coordination plane. In control experiments, parameters $A_{\mathrm{II}} = 165 \times 10^{-4}$ and $g_{\mathrm{II}} = 2.280$, obtained for Cu(II)–Resin 6 (containing amides of carboxylic acid only) system at pH 4.0 are significantly different from what was seen in the case of Resin 3–Cu(II) complexes. Now, the A_{II} parameter is 179×10^{-4} and g_{II} is 2.254. This is an indication that oxygen from the phosphonic groups and not from water must be bound at axial positions of N2O2 complexes formed by Resin 3. Otherwise parameters for both Resins 3 and 6, Cu(II) complexes would have been similar. Further increase of pH results in deprotonation of amino groups and since they become available there is a possibility of formation of complexes with N4 donor set as evidenced by sharp increase of A_{II} parameter.

Now, when we move to Cu(II)–Resin 1 system, in which phosphonic and amino groups are part of one functional group, the first clear difference is that the Resin 1 exhibits lower variation of Cu(II) complex forms. As can be seen in Fig. 4a and Table 3, there is no indication of complex with O4 donor set. The most probable explanation is that the Resin 1 exists in the form of zwitterion and that this makes formation of the aqua complex with phosphonic groups in axial position not possible. The first stable complex appears at pH 4.5 and has parameters similar to those listed in Table 3 for complex IIa of Cu(II)–Resin 3. In the same range complex II is also observed and it is observed at higher pH. The fact that it appears already at pH 4.0 and exists without the change of spectral parameters up to pH 10.0 suggests that N4 donor set around copper ion is realized by involvement of four amino groups and not by amidic nitrogen. Nitrogen atoms from amide are known to participate in complex formation but it takes place at pH close to 5 and higher [20]. At that point additional experiments were performed supporting the conclusion about lack of amidic nitrogen in coordination sphere around Cu(II). The amount of Resin 3 contacted with Cu(II) solution was decreased five times and under such conditions complex III, with characteristic EPR parameters, was detected at pH > 9.0 and its contribution to the overall

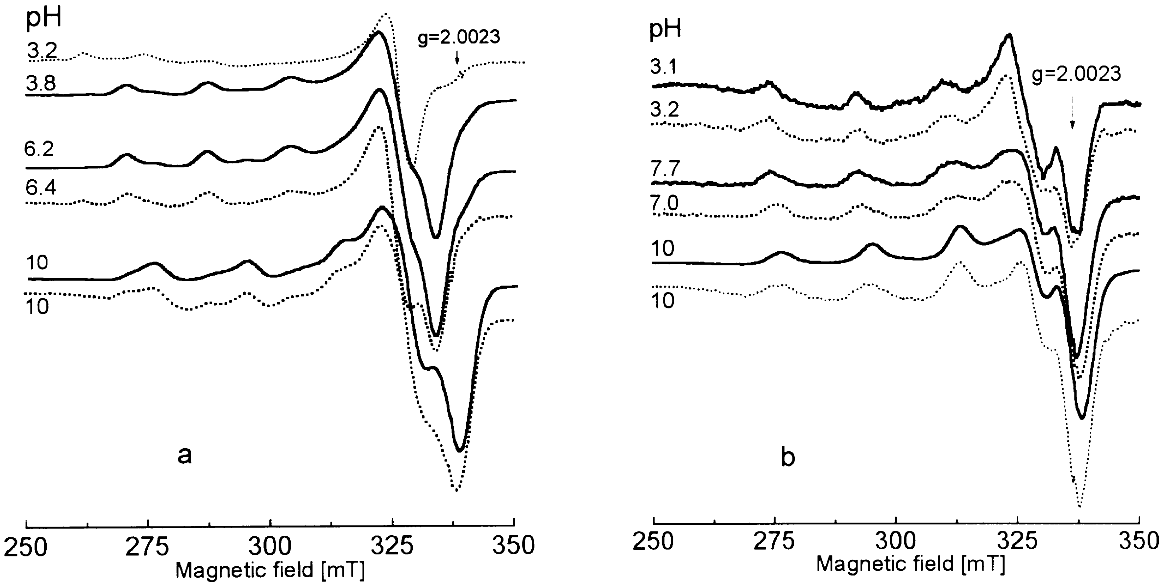

Fig. 4. (a) EPR spectra of the copper (II)–Resin 1 (solid lines) and copper (II)–Resin 3 (dotted lines) systems as a function of pH at 77 K. (b) EPR spectra of the copper (II)–Resin 2 (solid lines) and copper (II)–Resin 4 (dotted lines) systems as a function of pH at 77 K.

Table 3
EPR spectral parameters of copper (II)–resin complexes at 77 K

Resin	pH	g_{II}	A_{II} (10^{-4} cm^{-1}]	Complex	Donor set	Structure
1	4.5–10.0	2.276	173	CuL_2	N2O2	IIa
	4.0–10.0	2.210	196	CuL_4	N4	III
3	3.2–6.5	2.418	128	CuL_2	O4	I
	3.8–6.5	2.280	165	CuL_2	N2O2	II
	7.0–10.0	2.275	175	CuL_2	N2O2	IIa
	7.0–10.0	2.210	196	CuL_4	N4	III
2	3.0–8.0	2.338	184	CuL	N2O2	A
	5.0–10.0	2.215	186	CuL_2	N4	B
4	3.0–10.0	2.338	184	CuL	N2O2	A
	7.3–10.0	2.215	187	CuL_2	N4	B
5	3.0–5.0	2.415	128	CuL_2	O4	
6	4.0	2.254	179	CuL_2	N2O2	
	8.0–10.0	2.228	185	CuL_2	N3O	
7	4.0	2.229	182	CuL_2	N3O	
	5.0–10.0	2.210	192	CuL_2	N4	

Cu(II) uptake was smaller than in the case of previous experiments. This fact strongly indicates that complex III is formed by four nitrogens from primary amino groups. On the other hand, the parameters of N4 complex III ($A_{\mathrm{II}} = 196 \times 10^{-4}$ and $g_{\mathrm{II}} = 2.210$) reveal stronger in-plane coordination as compared to N4 complex formed by reference Resin 6 ($A_{\mathrm{II}} = 185 \cdot 10^{-4}$ and $g_{\mathrm{II}} = 2.228$ [12]. Schematically suggested (Fig. 5) the formation of hydrogen bond between phosphonic oxygen and amino hydrogen should be taken into account as additional effect stabilizing the complex III.

The proposed structures of complexes with N2O2 and N4 donor sets are presented in Fig. 5, respectively. Both complexes can be realized with either Resin 1 or 3. The stability of multi-member chelate ring, including both functional groups of Resin 1 (structure IIa), seems to be low, but even eight-membered ring was postulated to be formed with participation of two phosphonic groups and Cu(II) [21]. The other possibility is that monodentate phosphonic group of adjacent ligand may be involved in Cu(II) binding.

Apparently higher affinity of Resins 2 and 4 towards Cu(II) ions as compared to Resins 1 and 3 can be explained by ability of their amino groups to act as bidentate ligands. Since there are two amino groups, one secondary and one

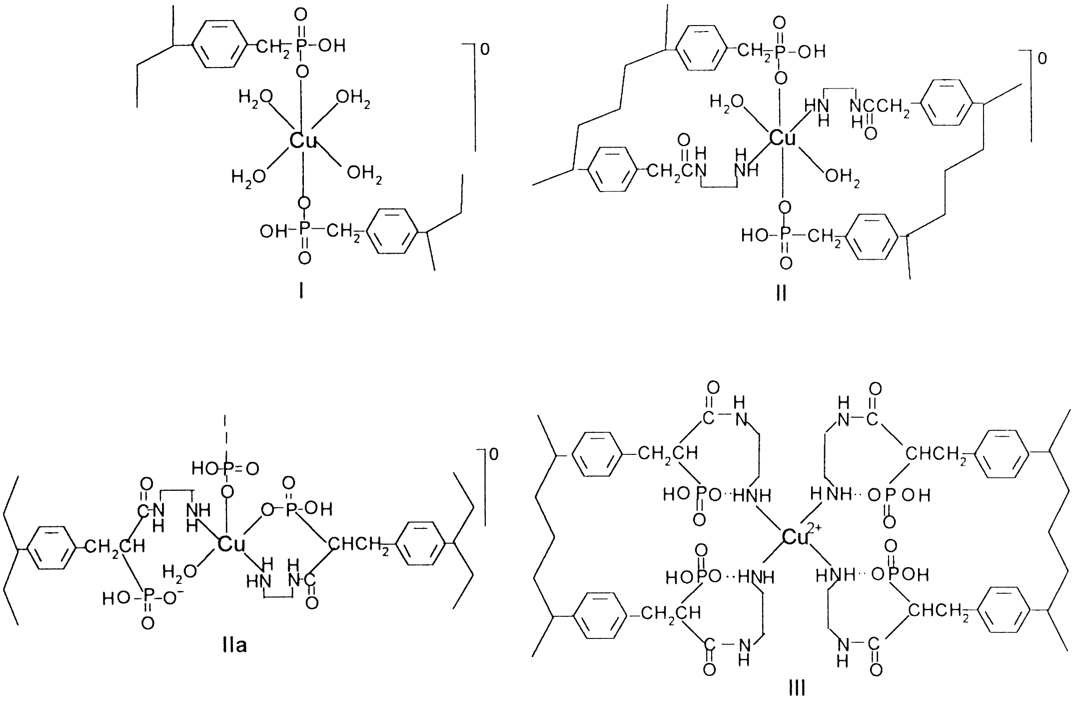

Fig. 5. Schematic presentation of the Cu(II) complexes with different donor sets realized by Resins 1 and 3.

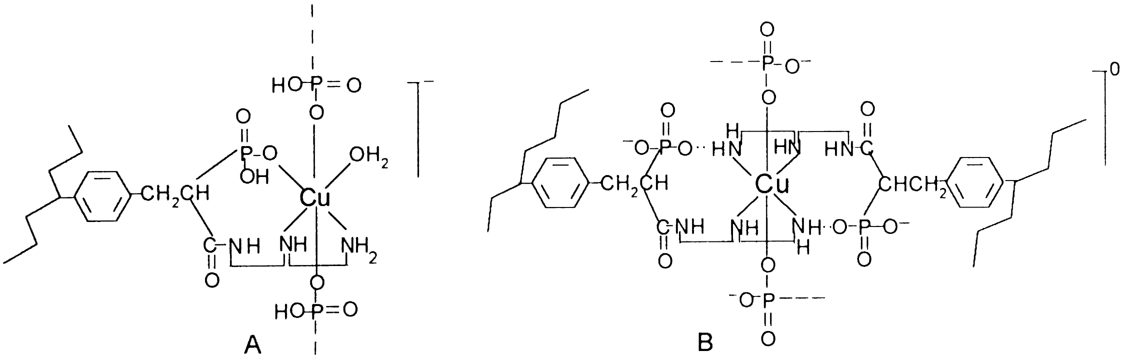

Fig. 6. Schematic presentation of the Cu(II) complexes donor sets realized by Resins 2 and 4.

primary, which can be involved in formation of N2O2 donor set around Cu(II) ion, it takes lesser amount of groups to form such coordination sphere. Therefore, type A complex in which N2O2 set exists, appears already at pH 3.0 and exists without change of parameters up to pH 8. In the pH range of 5.0–8.0 it exists in equilibrium with complex B having N4 donor set (Fig. 4b, Table 3). The latter one is dominant at pH above 7.0. A very similar situation is observed in the case of Resin 4. It should be noted here that neither of these resins form complexes with O4 donor set. Thus Resin 3 is different from Resin 4. It seems that the latter one, having longer chain ($-NHCH_2CH_2NHCH_2CH_2NH_2$) is able to form a zwitterionic structure even when amino and phosphonic groups are not parts of the same group. The proposed complex structures for these resins are presented in Fig. 6. Both Resins 2 and 4 can form these complexes but it seems that Resin 2 is more likely to be involved in B complex due to regular distribution of phosphonic and amino groups in its structure. It may also explain smaller binding capacity of Resin 2 towards Cu(II) ions since two ligands are needed for one metal ion in the CuL_2 complex. Spectra of both A and B complexes exhibit higher g_{II} and lower A_{II} parameters than the spectra of reference Resin 7 (having amide of carboxyl acid groups only) Cu(II) complexes taken in a control experiment. It may be interpreted as the evidence of weaker interactions between metal ion and ligands bound in Cu(II) plane resulting from the axial location of phosphonic groups (see Fig. 6).

4. Conclusions

In this paper it has been demonstrated that the obtained resins with substituted carbamylethylenephosphonate groups are able to remove Cu(II), Cd(II), Ni(II) and Zn(II) from their buffered solutions. Ion removal was far more effective at higher pH, where active groups were converted from a zwitterionic structure to dissociated phosphonic groups. At lower pH Zn(II), Ni(II) and in one case Cd(II) were not removed by the resins. All metal cations were removed by the reference resins, in which the same functional groups were deposited randomly within polymeric matrices. EPR investigations of resins Cu(II) complexes showed that only Resin 3, with phosphonic groups and amide of carboxylic acid groups placed separately and randomly within polymeric matrix, was able to form complexes with O4 donor set. This meant that only in the case of this resin a separation of active sites took place. Other resins, including investigated carbamylethylenephosphonate ones, have at low pH zwitterionic structures, inactivating phosphonic groups and making formation of complexes at lower pH more difficult.

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