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Synthesis and characterization of resins with ligands containing guanidinine derivatives. Cu(II) sorption and coordination properties

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Abstract

A new modification direction of acrylonitrile, vinyl acetate and divinylbenzene terpolymers (A, B) are presented. The aminolysis of nitrile groups of the terpolymers using ethylenediamine or hydroxylamine hydrochloride was a first stage of the modification. The resulting amine groups reacted with dicyandiamide (DCDA), cyanamide (CA) and sodium dicyanimide (SDC) in order to obtain the biguanidyl, guanidyl or nitrilguanidyl derivatives in the polymer side chain, respectively. The properties of all obtained resin such as water regain, nitrogen content, amine and carboxyl group concentration and sorption properties towards Cu(II) from nitric acid solutions were determined. The studies of IR spectra of all the resins were performed. Structures of ligand complexes with Cu(II) were studied using electron paramagnetic resonance spectroscopy.

Keywords: Guanidyl ligands; The Cu(II) sorption; EPR spectra of Cu(II) complexes

1. Introduction

The growing importance of chelating resins originates from their different applications in hydrometallurgy, preconcentration and recovery of trace metal ions, wastewater treatment. Ion-exchangers with porous structure are applied for purification of chemical compounds, also in non-aqueous solvents.

Resins and sorbents based on the acrylnitrile and divinylbenzene copolymer and on the acrylnitrile, vinyl acetate and divinylobenzene terpolymers have the application in these domains. Chemical modification of the polymers by hydrazine and diamines leads to the formation of ion-exchangers, applied to the sorption of organic compounds, enzyme immobilization and other bioactive substances, as well to the complexation of transition metals [1–15,24–26]. The Cu(II) sorption abilities are strictly depended on the resin structure, cross-linking degree and amine group concentration. The various resins with *N*-ethyleneaminoamide or amidoxime groups were presented previously [9,10,25] e.g. based on the acrylnitrile and divinylbenzene (20 or 10 wt% DVB) copolymer, which was characterized by high Cu(II) sorption (about 0.37 mmol/g) for resins with *N*-ethyleneaminoamide [9] and by Cu(II) sorption (about 3.5 mmol/g) for resins with amidoxime groups [10], as well based on the chloromethylated styrene and divinylbenzene (2 wt% DVB) copolymer, which showed the Cu(II) sorption at pH = 3.5 about 0.13 mmol/g and at pH = 5.7 about 0.27 mmol/g [25].

A variety of complexes formed by ligands containing the guanidine moiety (at first low-molecular weight compounds) have been reported. A majority of the reports detail complexes in which guanidinium cation plays role of a couterion and is not involved in co-ordination sphere of metal ion [1–3]. Cyanoguanidines have also received a great attention but they are co-ordinated mainly to the metal through the cyano nitrogen alone [4,5]. Infrared spectra of Co(II), Cu(II), Zn(II), Pd(II), Ni(II) and Cr(II) tetramethylguanidines complexes showed that the imine nitrogen of the ligands play role of the donor site [6].

Few publications are concerned with the complexes of transition metals with polybiguanide or biguanidine ligands attached to polymer support. East et al. [7] studied the sorption of Cu(II), Co(II) and Ni(II) ions by polymeric

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biguanide and its hydrochloride. It was demonstrated that the polymer forms coloured complex with a variety of metallic cations. When a blue $CuCl_2$ aqueous solution was added to an aqueous solution of polybiguanide and its hydrochloride, a rose–red colour appeared at first, and a precipitate formed on further addition. These rose–red copper complexes of polybiguanide hydrochloride once precipitated did not redissolve in distilled water. The rose–red insoluble copper(II) complex (Cu(II) ions with polybiguanide hydrochloride) contains two biguanide groups per copper(II) ion. A soluble coloured complex (Cu(II) with polybiguanide) is stable over a wide pH range (2–12.5).

In this paper, new ways of modification of nitrile groups (Fig. 1) in vinyl acrylonitrile acetate–divinylbenzene terpolymer (A) are described. The aminolysis of nitrile groups by ethylenediamine (EtDA) [8,9] or hydroxylamine hydrochloride (HA) [10] leading to ethyleneamidoamine and amidoxime groups, respectively, was a first state of terpolymer modification. The resulting amine groups were next converted to guanidine derivatives using dicyandiamide (DCDA), cyanamide (CA) and sodium dicyanimide (SDC) (Fig. 1). The structural characteristics of chelating ion-exchangers, their Cu(II) uptake ability and Cu(II) coordination properties based on EPR method are described.

2. Experimental

2.1. Materials

Copolymers of acrylonitrile, vinyl acetate and divinylbenzene were selected as the polymer supports. They were obtained from acrylonitrile, vinyl acetate and divinylbenzene by suspension polymerisation in the presence of solvent mixture: cyclohexanol–octanol in the volume ratio 9:1 (A) or cyclohexanol–2-ethylhexanol (B). During copolymerization, the volume ratio of monomers to diluents is kept 1:1 and DVB content at 10%. More details on preparation of AN/VA/DVB copolymers can be found in Refs. [11–13]. The copolymers contain nitrile groups, which can react with amine groups of modifying agent [10, 13,14] (Table 1). The functional groups provide active amine groups capable to react further with free nitrile or carboxyl groups.

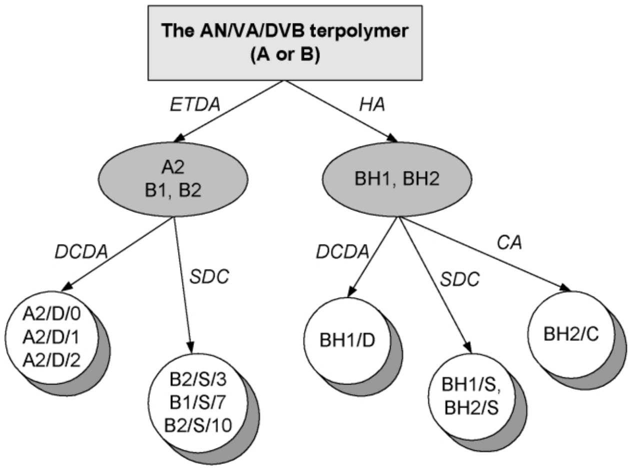


Fig. 1. The modification directions of acrylonitrile, vinyl acetate and divinylbenzene terpolymers.

2.2. Modification by dicyandiamide (DCDA)

About 1.5 g of prior-modified copolymer was swollen in 100 ml of distilled water for 24 h. The weight ratio of copolymers A2 or BH1 to DCDA was 1:5. The reaction with DCDA in the case of A2 was carried out with palmitic acid as the catalyst (leading to A2/D/1 and A2/D/2) or without catalyst (leading to A2/D/0) and in the case of BH1 only without catalyst (leading to BH1/D). Modification was carried out in the flask with reflux condenser at boiling point of reaction mixture for 10 h. The modified copolymers were separated from unreacted reagents and purified according to procedure I described below. To study a degree of hydrolysis of biguanidyl groups in the resin proceeding upon its storage in the water, the amine group concentration was determined three times (determination I, II, III) for the same resin sample.

2.3. Modification by sodium dicyanimide (SDC)

The copolymers B1, B2, BH1, BH2 were dried to the constant mass, next swollen in the SDC solution in *n*-butanol for 24 h. The weight ratio of prior-modified copolymer to SDC was 1:4. Reaction was carried out in the flask with reflux condenser at boiling point of reaction mixture for 16 h. After reaction, the products (B1(2)/S) were separated from unreacted reagents and purified according to following procedures:

- I (‘neutral’)—the product was washed with hot, distilled water
- II (‘acidic’)—first the product was bathed with hot HCl solution (about 0.001N), next was flooded with 1N HCl solution. It was bathed for 24 h with 0.001N HCl solution to neutralize amine groups (the pH should be about 5)
- III (‘basic’)—first the product was bathed with hot NH_3 solution (about 0.001N and pH close to 10), next it was washed from NH_3 using ethanol.

In the case of BH1/S and BH2/S the purification was carried out according to the neutral method.

2.4. Modification by cyanamide (CA)

The reaction of BH2 with CA was performed according to Section 2.3 (I neutral).

Table 1
Characteristics of resins after aminolysis by using ethylenediamine (EtDA) (A1, A2, A3, B1, B2, B3) or hydroxylamine hydrochloride (HA) (BH1, BH2)

Sample	Time of aminolysis (h)	Water regain (g/g)	Amine group concentration (mmol/g)		Carboxyl group concentration (mmol/g)	N (%)
			CS	H		
A1	42	4.5	2.60	–	0.80	13.3
A2	50	3.3	1.60		2.30	12.4
A3	54	3.3	2.40	–	1.20	10.6
B1	52	3.2	3.30	3.00	1.70	12.6
B2	52	3.4	2.30	2.20	0.58	12.3
B3	53	3.2	2.10	–	1.70	13.6
BH1	2	3.7	2.60	2.40	2.10	15.8
BH2	2	3.9	1.96	–	2.13	16.9

CS—determination using Colella–Siggia method; H—determination using Hecker method; N—the nitrogen content.

2.5. Methods

The water regain, W [g/g], was measured using a centrifugation technique (3000 rpm, 10 min). The total concentration of amine and carboxyl groups was determined according to Refs. [14,15], except that anhydrous ethyl alcohol was used for column washing. The content of amine groups was estimated from the measurement of HCl consumption. The nitrogen content was determined using Kejdalh's method. The IR spectra were recorded on SPECORD M-80 CARL ZEISS JENA (KBr pellets).

Sorption of Cu(II) ions was performed by the batch method. The swollen polymer sample was placed in 20 ml solution of $Cu(NO_3)_2 \cdot 3H_2O$ (concentration 1×10^{-4} or 2×10^{-4} M) in buffer acetate with pH between 4.0, 5.9 and 7.0. Cu(II) loaded sample was shaken for 48 h and separated. Cu(II) concentration was determined using spectrophotometric method (AAS) on atomic absorption spectrophotometer (PERKIN ELMER).

Electron paramagnetic resonance (EPR) spectra were performed at 77 K on a Bruker ESP 300E spectrometer at the X-band frequency and equipped with the Bruker NMR gaussmetter ER 035M and the Hewlett–Packard microwave frequency counter HP 5350B. The spectra were analysed by computer simulation program [16].

3. Results and discussion

In this work, the ways of modification leading to form the long ligands containing guanidyl or biguanidyl groups in the side chain of polymers are demonstrated. The functionalized polymers reveal good sorption properties towards Cu(II) ions from dilute solution of Cu(II) salts. The modification was carried out in two stages. We should pay attention at first to the structures of two of modified agents (DCDA and CA) and the amidoxime groups present in the side chain of resin after first stage of modification. According to X-ray diffraction studies of DCDA [17] the bond lengths of C–N and C=N in the guanidine fragment are equivalent indicating superposition of two tautomers: cyanoamine I and cyanoimine II. CA has also two tautomeric forms similar to DCDA [18] (Fig. 2). The tautomeric forms, stable in low-molecular compounds, were described for amidoxime [19,20]. Boudakgi [10] observed that during the aminolysis of nitrile groups two tautomers of amidoxime groups are formed; their content in the resultant resin is determined by the aminolysis conditions (Fig. 2). Obviously, the structure of the product depends on the tautomery of the reagents, amidoxime groups as well as DCDA, SDC and CA.

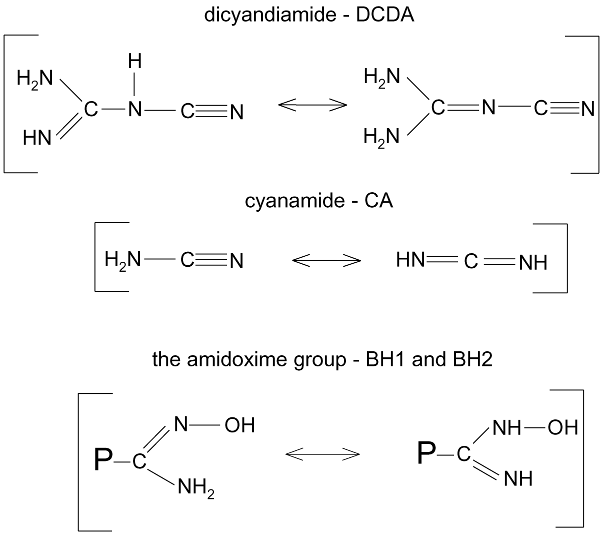


Fig. 2. The tautomeries of dicyanodiamide (DCDA) and the amidoxime groups attached to the resin.

3.1. Characteristic of resins after subsequent stage of modification

3.1.1. Aminolysis of acrylonitrile, vinyl acetate and divinylbenzene terpolymers (A or B) with ethylenediamine (EtDA) and hydroxylamine hydrochloride (HA)

The reaction between nitrile groups of polymer and amine groups of ethylenediamine (EtDA) occurs with a good efficiency leading to ethyleneamidoamine groups in the side chain of resulting A1(2,3) and B1(2). Furthermore, it is well known that nitrile groups undergo the hydrolysis to carboxyl groups; the hydrolysis degree increases with aminolysis time [12,13]. In the systems studied by us the cross-linking reactions with participation of all resulting groups occur. The efficiency of these processes appeared to be high, especially when the aminolysis proceeded longer then 40 h. The properties of resulting resins are shown in Table 1.

As described previously [11–13], cyclohexanol is a good solvent for terpolymer and has the highest influence on formation of the porous structure during the polymerization. Because of spherical shape, the branched 2-ethylhexyl alcohol is more active in increasing the polymer porosity than aliphatic alcohols with long chains. Terpolymer B has greater porosity and smaller density ($P = 0.639$, $d = 1,04$ g/cm^3) than polymer A ($P = 0.621, d = 1.12$ g/cm^3) [11–13]. Therefore, the aminolysis of the polymers proceeds with a higher efficiency for B than for A. As suggested previously [13], the nitrile groups are located mainly in the surface part of the polymer agglomerates that form porous grains. Their modification and hence introduction of bulkier, partly hydrated *N*-ethylamine groups may reduce the overall porosity of the ion-exchanger. The porosity characteristic of resin after modification by means of ethylenediamine was presented earlier [13].

The polymer with the amidoxime groups was obtained by aminolysis of nitrile groups of B by hydroxylamine hydrochloride. Both the hydrolysis of nitrile and amidoxime groups occurs next to the aminolysis of nitrile groups in this system. The ion-exchangers with amidoxime groups were described earlier [10]. The concentrations of the amidoxime and carboxyl groups formed in the modified BH type resins are presented in Table 1.

The changes in chemical composition of the resins during the aminolysis by EtDA or HA are illustrated by the IR spectra earlier [10,12,13]. As the degree of conversion increases, the band of the C=O stretching vibrations (at about 1720 cm^{-1}) and the band of the N–H deformation vibrations (at about 1632 cm^{-1} for A1(2) or B1(2) and at 1655 cm^{-1} for BH1(2)) appear and the intensity of band due to C≡N valence vibrations decreases (about 2240 cm^{-1}). The most characteristic bands of the amidoxime polymers are those from C=N stretching and from =N–O– stretching. The former is located at 1675–1650 cm^{-1}, and the latter at 920–945 cm^{-1}.

3.1.2. Characteristic of resins formed in reaction with dicyandiamide (DCDA)

The reaction of NH$_2$ groups (in the side chain of polymer) with nitrile groups of dicyandiamide (cyanoguanidine) (Fig. 3) was not yet studied. According to Tomasik [21], in the case of the first-order amines of low molecular weight, this reaction proceeds with protonation of amine groups of DCDA and acyliminoguanidyl (with biguanidyl moiety) groups are formed. The synthesis of polybiguanidine in reaction of DCDA nitrile groups with different amines was presented in Ref. [21]. As a result of reaction between amine groups of polyallylamine and guanyl-*O*-methylisourea hydrochloride the biguanidine groups are incorporated into the side chain of polymer [22]. On the other hand, the reaction between hydroxyl groups of the polymer and amine groups of DCDA is also possible; it leads in the first stage to unstable iminoethers, which may rearrange into ketoimines [22].

We suggest, according to the data presented below that in our systems the acylimineguanidyl and acyliminocarbamide groups (as a result of hydrolysis of biguanidyl groups) are formed next to biguanidyl groups (Fig. 3b and c). Two reactions between amidoamine groups of polymer and DCDA were carried out using palmitic acid as liquid–solid interface catalyst depending on the catalyst concentration. The influence of catalyst concentration on the resin properties is presented in Table 2. It is distinctly observed that the amine and carboxyl group concentrations after second stage of modification are significantly changed. In all cases, the amine group concentration increased about 25% mol. The carboxyl group concentration decreased and this loss is dependent on the amount of used catalyst. For weight ratio of catalyst to copolymer 1:7 (the A2/D/1 resin), the concentration of carboxyl groups decreased about 95% mol. Hence, it is very probable that the reaction between the carboxyl groups of polymer and nitrile groups of DCDA in the presence of catalyst (the A2/D/1 and A2/D/2 resins) (Fig. 3b) and the reaction between the amine groups of polymer and the nitrile groups of DCDA in the absence of catalyst (Fig. 3a) are dominant processes (the A2/D/0 resin). Furthermore, the amine group concentration decreased after next determinations on the same sample of resin (see A2/D/1 and A2/D/2, determinations: I, II, III). It suggests that the imine groups of biguanidine derivatives in the side chain of polymer hydrolyses to carbonyl groups, leading to the acylimineguanidyl and acyliminecarbamido derivatives (Fig. 2c).

In Table 4 the characteristics of BH1/D is presented. The amine group concentration of BH1/D decreased about 77% mol, whereas the nitrogen content increased about 2.5%. At the same time, the concentration of carboxyl group remains almost unchanged upon the modification (the difference was about 8%). The data indicate that the cyanurea groups (similarly to biguanidyl groups) can hydrolyse to carbamidonitrile and the reaction between the hydroxyl groups of BH1 and the amine or nitrile groups of DCDA is also

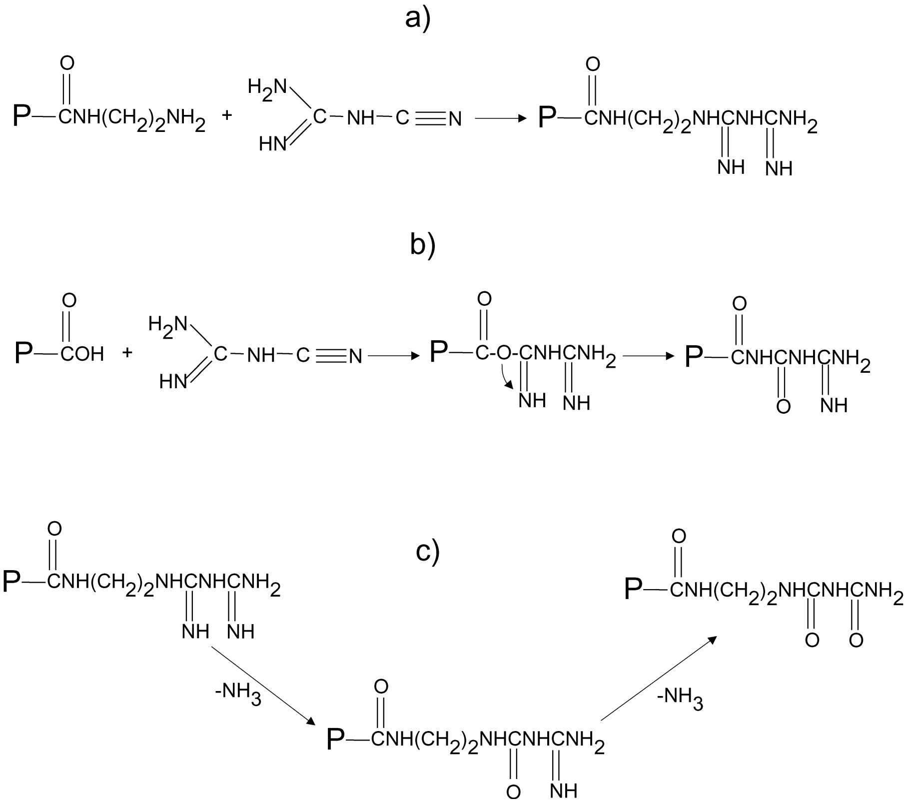
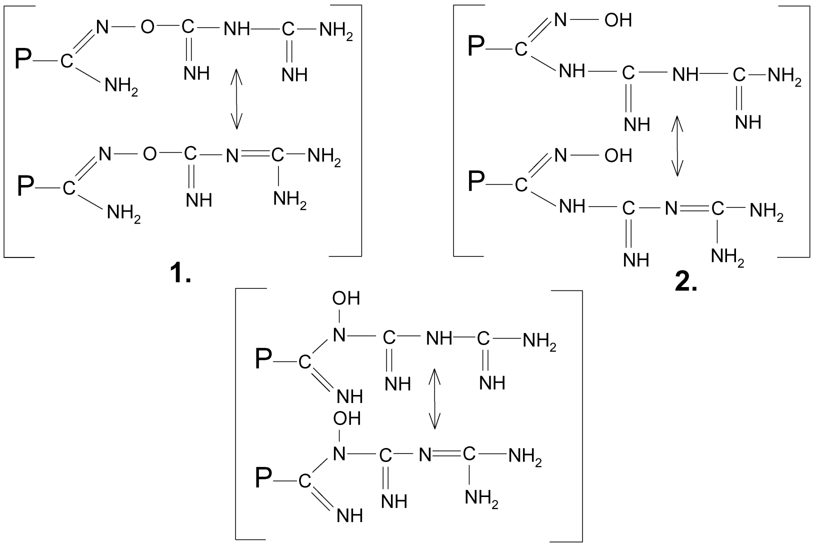


Fig. 3. A scheme of the reactions occurring in the DCDA–A systems: (a) between the amine groups of A and nitrile groups of DCDA; (b) between the hydroxyl groups of A and nitrile groups of DCDA; (c) hydrolysis of biguanidine derivatives.

probable. The proposed scheme of the reaction products is shown in Fig. 4.

The studies of water regain provide additional information. The nature of the resin changed from weakly hydrophilic to strongly hydrophilic (the water regain increased about 70%).

In order to confirm the proposed reaction, the measurements of IR spectra of the resin samples were performed. A detail comparative interpretation of the IR spectra limited to 1800–1500 cm^{-1} was made for the A2/D/0, A2/D/1, A2/D/2 (Fig. 5a) and BH1/D resins (Fig. 5b). However, in the region from 1750 to 1600 cm^{-1} only wide band is observed. This band should be treated as a result of the overlapping of several bands. The following bands were



1.

2.

3.

Fig. 4. The most important products occurring in the DCDA–BH1 system (1, 2, 3 are the couple of two tautomeric forms).

Table 2
Characteristics of resins after modification of dicyandiamide (DCDA) in the function of catalyst content (palmitic acid) used during modification

Sample	Amount of catalyst during modification (%)	Water regain (g/g)	Amine group concentration before reaction (mmol/g)	Amine group concentration after reaction (mmol/g)			Carboxyl group concentration after reaction (mmol/g)	N (%)
				I	II	III		
A2/D/0	0	3.7	1.60	2.00	–	–	2.11	11.1
A2/D/1	14	3.3	1.60	2.00	1.20	1.00	0.12	9.7
A2/D/2	23	3.2	1.60	1.80	1.30	1.20	0.92	12.9

I—first determination, method of Colella–Siggia; II—second determination, method of Hecker; III—third determination, method of Hecker.

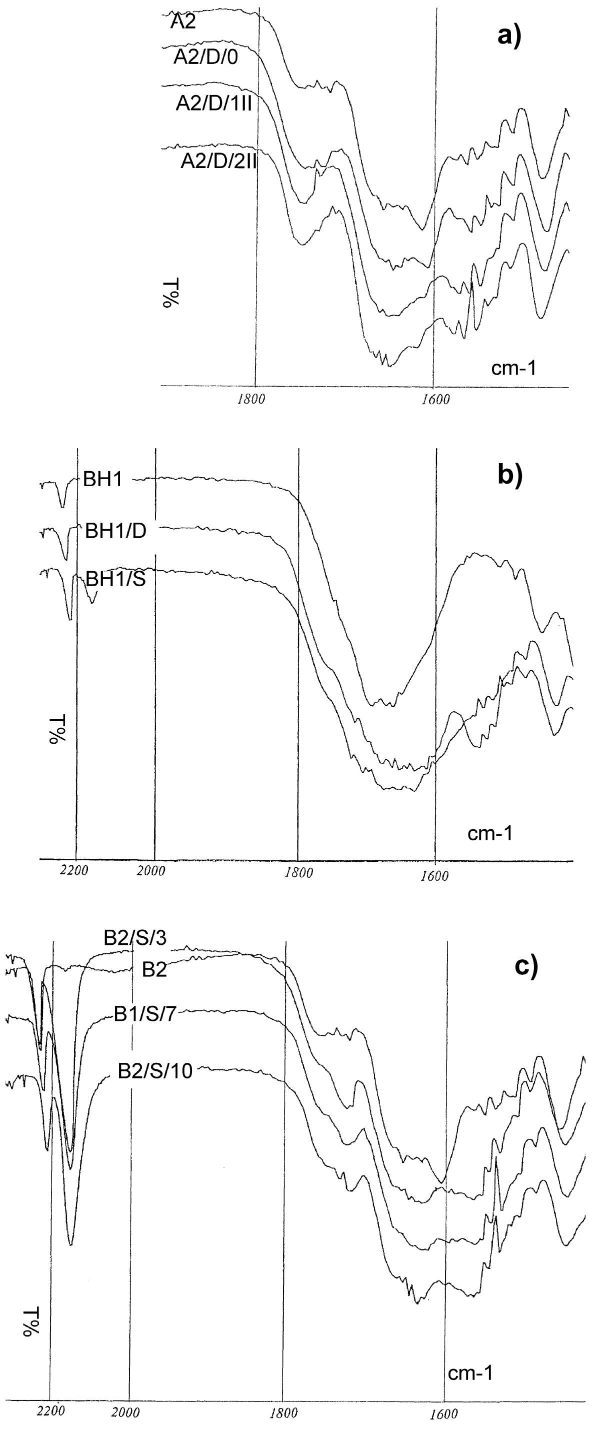


Fig. 5. IR spectra for: (a) A2, A2/D/0, A2/D/1II and A2/D/2II; (b) BH1, BH1/D and BH1/S; (c) B2, B2/S/3, B1/S/7 and B2/S/10.

taken into account; the C=O valence vibration band at 1760–1740 cm^{-1} for the A2/D or at 1720 cm^{-1} for BH1/D, the wide and strong N–H band at 1620–1590 cm^{-1} for A2/D or 1560 cm^{-1} for BH1/D and deformation vibration band of C=N at 1665–1650 cm^{-1} for A2/D or at 1654 cm^{-1} for BH1/D. The most important band at about 1640 cm^{-1}, characteristic of the biguanidyl or guanidyl group vibration, appears in all IR spectra. In the case of A2/D resins, along with increasing catalyst concentration, the absorption of the band (at 1610 cm^{-1}) decreases and of the band at 1760–1740 cm^{-1} increases. It indicates that the hydrolysis of imine groups to carbonyl groups took place. At 2240 cm^{-1} the band of nitrile group vibration with unchanged intensity, as compared to that observed for starting resin (A2 or BH1), is seen. It shows that nitrile groups of the resins were not involved in the reaction with DCDA.

3.1.3. Characteristic of resins formed in reaction with sodium dicyanimide (SDC)

The reaction mechanics of sodium dicyanimide (SDC) with primary amine groups should be similar to that of DCDA. Schematically, the reaction leading to the cyanoguanidyl groups in the side chain of resin is shown in Fig. 6. The reaction between the nitrile groups of SDC and the amine groups of polymer as a method of polybiguanidine preparation was presented in Ref. [21]; as a result the cyanoguanidyl groups in the side chain of polymer were formed. We should emphasize that the imine groups of the cyanoguanidyl groups can also hydrolyse to the cyanocarbamide groups [22] (Fig. 6).

Modification of B by SDC gives three series of the products. Although the way of synthesis was similar, the water solutions at different pH were used for the product purification. It can be observed (Table 3) that the amine and carboxyl group contents are smaller in the B/S type resins than in B1(2) resins and the concentration of the amine group is higher when the products were treated by water solutions at pH = 7 (the B1/S/7 resin) and pH = 10 (the B2/S/10 resin) than at pH = 3 (the B2/S/3 resin). On the other hand, a significant decrease in the amine group content and almost unchanged nitrogen content (in comparison to starting B1 or B2 samples) imply that hydrolysis and the cross-linking reaction take place in a significant degree. Furthermore, the water regain of the product is about 70% lower (Table 3) than for B1 or B2 supporting the cross-linking process.

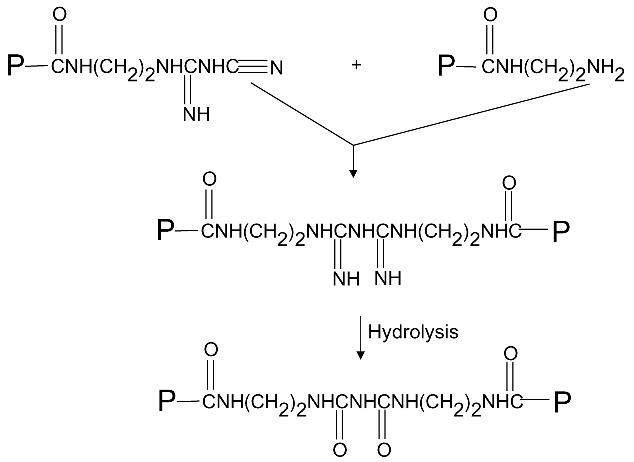


Fig. 6. Scheme of the cross-linking reactions occurring in the SDC–B systems.

Table 3
Characteristics of resins after modification of sodium dicyanimide (SDC) in the function of pH medium during modification

Sample	pH medium during modification	Water regain (g/g)	Amine group concentration before reaction (mmol/g)	Amine group concentration after reaction (mmol/g)		Carboxyl group concentration after reaction (mmol/g)	N (%)
				I	II		
B2/S/3	About 3	1.1	2.20	0.90	0.70	0.70	13.1
B1/S/7	About 7	0.7	3.00	1.40	–	0.70	14.1
B2/S/10	About 10	0.8	2.20	1.20	1.10	0.80	16.0

I—amine group concentration determinated using method of Colella–Siggia; II—amine group concentration determinated method of Hecker.

Modification of BH1 and BH2 using sodium dicyanimide (SDC) may be based on the known [7,21,22] reactions between the nitrile groups of SDC and the amine and/or the hydroxyl groups (Fig. 7) of amidoxime. Hence, the processes should lead to the cyclic as well as to the linear products, respectively. The cyclic products may be also formed as a result of reaction between the amine and carboxyl groups of amidoxime moiety. On the other hand, the amidoxime groups undergo the hydrolysis leading to two hydroxyl groups [10,14], which can next react with both nitrile groups of SDC giving cyclic structures. In Table 4 the characteristics of the BH1/S and BH2/S are presented. The amine group concentrations in BH1/S and BH2/S are reduced about 80% in comparison to their concentration in starting BH1 and BH2, respectively. The carboxyl group concentration is not changed precluding the reaction between the nitrile groups of SDC and carboxyl groups of BH1 or BH2. A decrease in water regain suggests that the cross-linked reaction in the system occurred. This may be due to the reaction of two nitrile groups of SDC with two different amine and/or hydroxyl groups giving the cross-linked biguanidine bridge.

A comparison of the IR spectra of the resulting resin (B2/S/3, B1/S/7, B2/S/10 or BH1(2)/S) (Fig. 5b and c) and the starting resins (B1(2) or BH1(2), respectively) reveals substantial differences within 1800–1500 cm^{-1}. New band at 1640 cm^{-1} for B1(2) and at about 1650 cm^{-1} for BH1(2), characteristic of the $-C{=}NH$ groups, is seen. The absorption of the bands due to NH deformation vibrations at 1540 cm^{-1} increases and at 1612 cm^{-1} decreases. However, at 1720 cm^{-1} the C=O stretching vibration band appears for B1(2) samples. In the case of BH1(2) the intensity of the band associated with N–H deformation vibration at 1632 cm^{-1} decreases suggesting that the hydrolysis of amidoxime and cyanoguanidyl took place in the systems studied. A region from 2300 to 2100 cm^{-1} seems to be also interesting. The band at 2240 cm^{-1} (characteristic of nitrile groups) is split into two bands: first characteristic of nitrile groups at 2239 cm^{-1} (shifted towards the lower wave number) and second at 2177 cm^{-1} characteristic of $-C(=NH)-CN$ groups. The intensities of these bands are the highest for B2/S/10 and BH1(2)/S. We suppose that the hydrolysis of cyanoguanidyl groups of B2/S/10 takes place in smaller extent than in the case of B2/S/3 and B1/S/7.

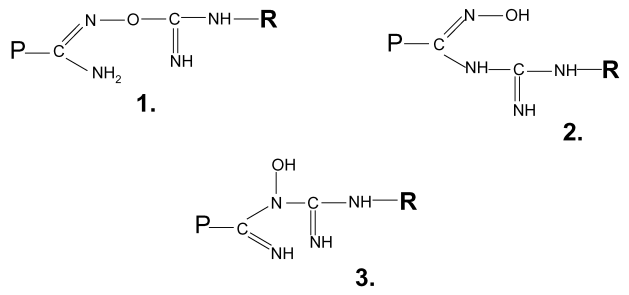


Fig. 7. The most important ligands formed in the SDC–BH1(2) or CA–BH2 systems (R = H for CA and C≡N for SDC).

3.1.4. Characteristic of resins formed in reaction with cyanamide (CA)

To form the guanidine groups in the side chain of polymer, the reaction of BH2 with cyanamide (CA) was performed. The process route (Fig. 7) apparently depends on the tautomeric structure of CA and amidoxime groups, similarly to that postulated in the case when DCDA reacts with BH1.

For BH2/C resin lower amine group concentration and high loss of nitrogen in comparison with BH2 is observed (Table 4). This is probably caused by formation of the cyclic structures; a decrease of water regain for 45% and decrease in the concentration of the carboxyl group support the supposition.

The IR spectrum of BH2/C shows new band at 1669 cm^{-1} due to C=N vibration characteristic of guanidine groups. A disappearance of the band characteristic of N–O groups at 920 cm^{-1} and lower absorption of a band assigned to N–H at 1566 cm^{-1} probably results from hydrolysis of amidoxime groups. This is confirmed by the nitrogen content loss and increase in the carboxyl group concentration.

3.2. The sorption properties of the resins towards Cu(II) ions

Apart from the polymer structure (the porosity, the cross-linked degree, the water regain) the exterior factors e.g. pH, the ion concentration in solution, the kind of couterion may influence the sorption properties of the studied chelating ion-exchangers.

Cu(II) ions were sorbed from $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution of 1×10^{-4} M concentration. The molar ratio of ligands to Cu(II) was kept above 10. In Table 5 the Cu(II) sorption properties are presented. Uptake of Cu(II) ions apparently increases with increasing concentration of amine groups in the resin.

The sorption ability of the samples is presented for four groups depending on the nature of the ligands.

The resins from group 1 (Table 5) were prepared in the first stage of modification by use ethylenediamine (A1, A2, B1 and B3). The B1 and B3 samples showed higher sorption and distribution coefficient as compared to A1 and A2. Especially low values of the parameters are observed for A2. Terpolymer B has looser structure than A, especially in swollen stage. In addition, the aminolysis of B as well as the Cu(II) sorption proceed with higher efficiency than for A. The B1 and B3 resin have the same carboxyl group concentration (1.7 mmol/g) and water regain (3.2 g/g) but for B3 the concentration of amine groups is lower. For this reason the Cu(II) sorption for B1 at pH = 4.0 is higher than for B3. Furthermore, B3 resin is most likely more cross-

Table 4
Characteristics of resins with amidooxime groups after modification of dicyanodiamide (DCDA), cyanoamide (CA) and sodium dicyanimide (SDC)

Sample	Modificated agent	Water regain (g/g)	Amine group concentration before reaction (mmol/g)	Amine group		concentration after reaction (mmol/g)	
	Carboxyl group concentration after reaction (mmol/g)	N (%)					
				CS	H		
BH1/D	Dicyandiamide	6.0	2.60	0.60	0	2.20	17.1
BH2/C	Cyanamide	2.2	1.96	0.70	–	3.20	12.2
BH1/S	Sodium dicyanimide	2.0	2.60	0.50	0.20	2.30	13.4
BH2/S	Sodium dicyanimide	1.9	1.96	0.30	–	2.50	16.8

I—amine group concentration determinated using method of Colella–Siggia; II—amine group concentration determinated method of Hecker.

linked than B1 due to higher stiffness of B3 structure and Cu(II) diffusion is less efficient.

The resins of A2/D type (prepared from A2 and DCDA) reveal higher Cu(II) sorption than the starting A2 (Table 5, group 2). Although the biguanidyl groups there are next to the carboxyl groups in resin A2/D/0 (Table 2), the concentration of carboxyl groups is much lower for A2/D/1 and for A2/D/2. In spite of these differences the Cu(II) sorption for all A2/D resins are close to each other and is not higher than 0.66 mg/g.

The studies of Cu(II) sorption by the resins prepared from B1 or B2 in the reaction with SDC (Table 5, group 3) reveal the highest sorption and distribution coefficient for B1/S/7 while for B2/S/3 the lowest, although their sorption is smaller than for starting B1 or B3. According to our suggestion above, the resins contain the cyanoguanidyl groups next to the cyancarbamide groups. The presence of the nitrile groups in the end of the side chains and higher cross-linking (than for B1 and B2) of the resultant resins can additionally interfere with the diffusion of Cu(II) ions. As the nitrogen content increases and amine groups decreases most effectively for B2/S/3 it may the reason that its Cu(II) sorption is lower. Although the cross-linking causes the stiffness of resin structure to increase, it leads also to formation of the biguanidyl groups and the latter effect should be treated as a reason that resins of B2/S type reveal in general higher Cu(II) uptake than B.

The group 4 (Table 5) consists of the resins prepared by different first stage of modification than these above. The BH1/D resin has much higher water regain, much lower amine group concentration and a little higher nitrogen content than BH1 resin. The Cu(II) sorption for resin BH1/D

Table 5
The sorption properties of the obtained resins

Group	Resin	pH	Sorption S (mg/g)	Sorption $S \times 10^2$ (mmol/g)	Distribution coefficient lgK
1	A1	4.0	0.55	0.99	1.95
	A2	4.0	0.31	0.55	1.70
	B1	4.0	0.99	1.56	2.21
	B3	4.0	0.64	1.00	2.02
2	A2/D/0	4.0	0.48	0.76	1.89
	A2/D/1II	4.0	0.47	0.75	1.90
	A2/D/1III	4.0	0.66	1.04	2.06
	A2/D/2II	4.0	0.39	0.61	1.81
	A2/D/2III	4.0	0.47	0.74	1.90
3	B2/S/3	4.0	0.33	0.51	1.74
	B1/S/7	4.0	0.65	1.02	2.04
	B2/S/10	4.0	0.53	0.83	1.95
4	BH1	4.0	0.89	1.40	2.17
	BH2	5.9	2.37	3.70	3.69
	BH2	7.0	4.48	7.00	3.07
	BH1/D	4.0	1.30	2.05	2.50
	BH1/S	4.0	1.27	2.01	2.56
	BH2/S	5.9	0.85	1.33	3.78
	BH2/S	7.0	0.74	1.16	3.03
	BH2/C	5.9	2.14	3.34	4.16
	BH2/C	7.0	1.74	2.72	3.35

is higher than for resin BH1. These structures bring about the loosening of polymer chains leading to increase in water regain. It makes easier the Cu(II) diffusion from the solution to the bead. In the case of BH1/S, BH2/S and BH2/C the situation is similar to BH1/D, but the water regain decrease after modification with SDC or CA what is probably caused by cross-linking processes in the resins modified by SDS. However, in the case of BH2/C, the decrease in the concentration of amine group is probably due to the hydrolysis of imine groups in the guanidyl ligands. Unexpected properties exhibit BH1/S and BH2/S. In this case, the influence of pH solution on the Cu(II) sorption was studied. For the resins with the amidoxime groups (BH1, BH2) the sorption increases with the increase of pH solution; BH2 sample at pH = 7.00 shows the highest sorption and distribution coefficient. The Cu(II) sorption for BH1/S at pH = 4.0 is higher than for BH1, however for BH2/S at pH = 5.9 is lower than for BH2. The highest Cu(II) sorptions show BH2/C at pH = 5.9 and BH1/S at pH = 4.0.

It can be observed that the resins after first stage of modification (with *N*-ethyleneamidoamine as well as with the amidoxime groups) showed the sorption higher than those after the second stage of modification. All of resins from group 4 has the Cu(II) sorption much higher than the sorption of the resins from groups 2 and 3 prepared in the same second stage of modification with DCDA or SDC.

3.3. EPR studies of Cu(II) complexes with the resin functional groups

The EPR spectra of the complexes formed between functional groups of the resins and Cu(II) ions are characteristic of tetragonal geometry of the complexes with $d_{x^2-y^2}$ ground state (Fig. 8). An anisotropic character of the spectra observed at 295 and 77 K implies that Cu(II) are bound to the immobilized functional groups of the side polymer chains. The main components of tensors A (being the measure of hyperfine interaction between copper nuclei spin ($I = 3/2$) and unpaired electron) and g (electron Zeeman splitting factor) of the spectra reveal the relations $A_{\parallel} \gg A_{\perp}$ and $g_{\parallel} \gg g_{\perp}$ implying that the parameters $g_{\parallel}$ i $A_{\parallel}$ are particularly sensitive to the change of coordination sphere in Cu(II) plane [23].

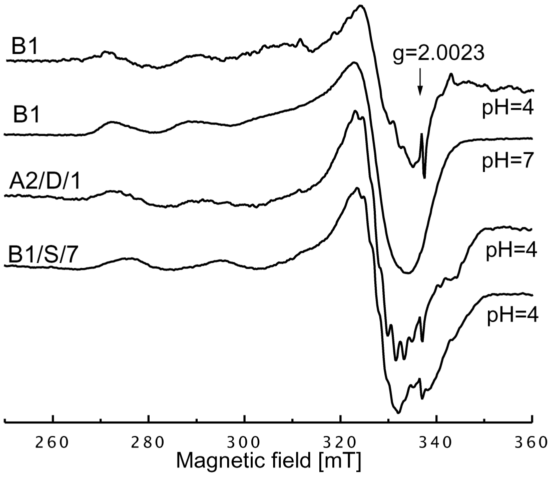


Fig. 8. EPR spectra of the complexes formed between Cu(II) ions and the functional groups of B1, A2/D/1 or B1/S/7 resins at 77 K and different pH.

The EPR spectra for Cu(II) loaded B1 (Fig. 8) are in a good agreement with those observed for the Cu(II) complex with $-CONHCH_2CH_2NH_2$ incorporated into polymer matrix [24]. The spectrum at pH ~4 corresponds to two complexes with parameters $A_{\parallel} = 177 \times 10^{-4}\ cm^{-1}$; $g_{\parallel} = 2.258$ and $A_{\parallel} = 183 \times 10^{-4}\ cm^{-1}$ i $g_{\parallel} = 2.225$ in equilibrium. The parameters of the first dominant complex should be assigned to N2O2 donor set around Cu(II) plane and the second to N3O or N4. The relation between the complexes contribution is not dependent upon pH, at pH = 7 an increase in the intensity of the signals is only observed. It indicates that amido nitrogens are in less extent involved in coordination in this case and CuL_2 and CuL_3 (or CuL_4) type complexes are formed by monodentate nitrogen donors of the ligands.

The Cu(II) complexes immobilized by A2/D/1 exhibit characteristic EPR spectrum observed usually for the resins with the ligands providing guanidyl nitrogens as donors able to bind Cu(II) ions. Similar parameters ($A_{\parallel} = 184 \times 10^{-4}\ cm^{-1}$; $g_{\parallel} = 2.250$) as well as the hyperfine structure due to nitrogen atoms suggests the same coordination mode with N2O4 donor set around Cu(II) plane. Oxygen donors are most likely provided by carboxyl groups present in the resin A broad peaks of parallel orientation (probable from two overlapping lines) and a weak additional peak at the highest magnetic field may suggest the small content of the second type complex with parameters similar to those characteristic of the complex formed by Cu(II) loaded B1/S/7 resin.

The parameters $A_{\parallel} = 192 \times 10^{-4}\ cm^{-1}$ and $g_{\parallel} = 2.213$ of the spectrum of Cu(II)–B1/S/7 system at pH = 4 should be ascribed to N4 donor set around Cu(II) ion and resemble quite closely those found for the complexes with two bidentate $-NHCH_2CH_2NH_2$ groups [24]. On the other hand, the hyperfine splitting due to nitrogen donors (seen on the high field lines) is typical for guanidine ligands [25] as well as pH is too low to achieve deprotonation of amide nitrogen of the ligands bearing guanidine or biguanidine groups necessary to involve them in Cu(II) binding. Taking into account the characteristics of A2/D/1 and B1/S/7 in relation to the starting resins A2 and B1, it is clear that the reaction of B1 with dicyandiamide leads to more effective modification to the biguanidine derivatives providing nitrogen donors.

The EPR spectrum of Cu(II) complexes formed as a result of Cu(II) uptake by BH (Fig. 9) corresponds to $A_{\parallel} = 195 \times 10^{-4}\ cm^{-1}$; $g_{\parallel} = 2.230$ at pH ~4, and to $A_{\parallel} = 199 \times 10^{-4}\ cm^{-1}$; $g_{\parallel} = 2.208$ at pH ~7 typical for the complexes with two amidoxime ligands [26]. This coordinate mode leads to very stable chelate rings with aromatic

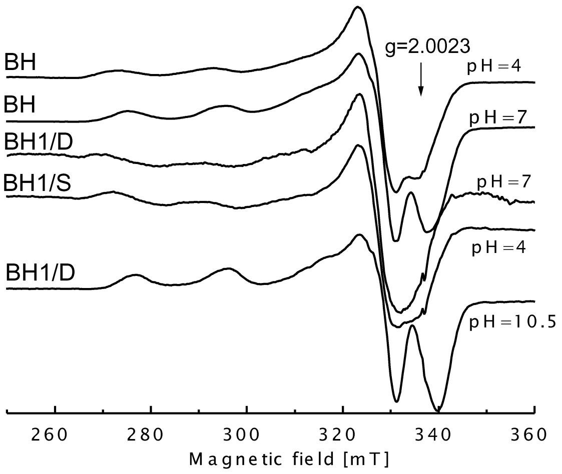


Fig. 9. EPR spectra of the complexes formed between Cu(II) ions and the functional groups of BH, BH1/D and BH1/S/7 at 77 K and different pH.

character. At higher pH, deprotonation of oxygens results in higher negative charge affecting the spectral parameters in the observed trend.

Cu(II) loaded BH1/D samples exhibit EPR spectrum with poor resolution of copper hyperfine structure and parameters $A_{\|} = 180-186 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $g_{\|} = 2.266$ which are apparently different from the spectrum assigned to the complexes observed for starting amidoxime containing polymers. This effect may be associated with formation of the complexes with nitrogen donors of the guanidyl type groups. A much smaller intensity of the EPR signals than in BH1 is in agreement with lower content of the amine groups; it was postulated that the amines participate in the cyclization process. It is noteworthy that increase of pH above 10 of the solution in equilibrium with BH1/D for a few days results in EPR spectrum of apparently stronger intensity with feature and parameters typical for the complexes with two amidoxime ligands, observed in the starting BH1 resins. Apparently, the hydrolysis of the final groups (incorporated due to modification of amidoxime groups) occurs. Similar effect caused by alkalisation is observed for BH1/S. The intensity and parameters of the spectrum of BH1/S at pH = 4 are close to those observed for Cu(II) complexes with guanidyl groups of BH1/D ($A_{\|} = 180 \times 10^{-4}\ \mathrm{cm}^{-1}$; $g_{\|} = 2.255$) suggesting close nature of the resins BH modified by SDS and DCDA.

4. Conclusion

- The resins with biguanidyl, acylimineguanidyl and acyliminecarbamido groups were be prepared during the modification of resins with ethyleneamidoamine groups using DCDA (A2/D/0, A2/D/1 and A2/D/2, respectively).
- The resins with the cyanoguanidyl or cyanocarbamido groups were prepared during the modification of resins with ethyleneamidoamine groups using SDC (B2/S/3, B1/S/7 and B2/S/10). The hydrolysis degree of cyanoguanidyl groups was controlled by pH of washing solution (the higher pH the lower degree of hydrolysis).
- The participation of cross-linking reactions is probably the higher in the case of B1(2)/S and BH1(2)/S samples. The cross-linking leads to the formation of biguanidyl groups in resin.
- The resins with amidoxime groups showed the higher Cu(II) sorption than the resins with ethyleneamidoamine groups.
- All of the obtained groups in the resins (biguanidyl, guanidyl, nitrylguanidyl, amidoxime) can undergo hydrolysis into acyliminecarbamido, cyanocarbamido or carboxyl groups, respectively. The low pH was conducive to the hydrolysis.
- The EPR spectra indicated different properties of Cu(II) complexes formed by the subsequently modified resins confirming the incorporation of new functional groups after every stage of the resin modification and showed that Cu(II) coordination of the functional groups are apparently dependent on pH.

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