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Synthesis and some sorption properties of anion exchangers bearing ligands of different length with guanidyl and biguanidyl end groups

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Abstract

In this work the influence of ligands length with guanidyl and biguanidyl end groups on the performance of anion exchangers is presented. These anion exchangers are synthesized in a two-step reaction. Firstly, the aminolysis of chlorine in a copolymer of vinylbenzyl chloride (VBC) and 2 wt% of divinylbenzene (DVB) with hexamethylenediamine (HMDA) or diethylenetriamine (DETA) is conducted. Thus obtained amine derivatives are subsequently reacted with cyanamide, carbodiimide or sodium dicyanamide. It is found that the most convenient method of biguanidine group introduction into polymer matrix is the reaction of amino groups with sodium dicyanamide. Properties of resins are studied using Cu(II) ions as a spin probe detected by EPR method. A higher complexing ability towards Cu(II) showed by anion exchangers with DETA ligands (DETA resins) is due to chelating function of their ligands. The anion exchanger with HMDA ligands (HMDA resins) requires higher pH (about 7) to provide sufficient number of deprotonated nitrogen donors of monodentate ligands for sorption of Cu(II). The ligands length and their hydrophilicity do not change significantly sorption properties of resins towards dicyanoaurate and tetrachloroaurate.

Keywords: Anion exchangers with guanidyl groups; Gold sorption; Copper complexing

1. Introduction

There are two major methods of gold recovery: gold cyanide extraction using active carbon or polymeric resin in pulp and reclaiming of gold from secondary sources.

Application of ion exchange and sorption technology (i.e. resin in pulp) in both methods is gaining a lot of attention due to the selectivity of these processes. The concentration of gold in exploited earth's crust layer is in the range 2–5 ppm or even smaller. Simultaneously with gold cyanide extraction, suitable recycling methods were developed, because about 40% of gold is recovered from waste materials. Sorption based separation processes are not energy intensive and can thus be applied to low-grade mineral resources and to recovery of valuable metals from secondary resources.

Ion exchange is based on the distribution of soluble ions between an aqueous solution and a reactive polymer containing selective ligands. Equilibrium sorption and desorption depends on the external condition, i.e. the solution concentration, its pH, functional groups to ions ratio. However, the most important influence on sorption has the internal structure of ion exchangers and character of ligands end groups, which coordinate or chelate metal ions [1–3].

In our previous work we presented the literature data and demonstrated that ion exchangers with ligands having guanidyl end groups revealed affinity to dicyanoaurate anions [4–9]. This high affinity was ascribed to a very high pK_α of guanidine—13.4. Substituted guanidyl groups and biguanidine ligands showed better selectivity than primary amino groups [8,9].

The sorption of tetrachloroaurate was carried out from acidic solution on a weak-base anion exchanger, because gold complexes with strongly basic anion exchangers have been too stable. Resins with nitrogen atom containing ligands such as amidoxime [10,11], phenylendiamino [12], pyridylamino [13,14], imidazoline and its derivatives [15,16], hydrazone [17,18], piperazine and its derivatives [3,19], as well as sulfur [20–23] or phosphorus [24] atoms containing groups were used for the sorption of tetrachloroaurate. A lot of commercial anion exchangers were also tested. The sorption depends on chemical

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Table 1
Characteristics of anion exchangers with HMDA modified ligands (Z_c—anion exchange capacity)

Symbol	Water regain (g g^{-1})	N (mmol g^{-1})	Cl (mmol g^{-1})	Z_c (mmol g^{-1})	Z_L (mmol g^{-1})
HMDA	2.43	4.9	4.7	5.1	2.5
HMDA/CA1	2.46	5.3	4.8	4.8	2.4
HMDA/CA2	2.27	6.0	4.9	5.0	2.5
HMDA/CA3	1.72	10.2	4.0	3.8	1.9
HMDA/MCA	1.01	7.5	1.9	2.2	1.1
HMDA/DCCI/1	1.76	4.8	4.5	4.6	2.3
HMDA/DCCI/2	2.10	4.9	4.4	4.4	2.2
HMDA/SDC1	0.24	16.2	0.3	0.3	0.2
HMDA/SDC2	0.62	10.8	2.3	2.7	1.4
HMDA/U1	0.38	13.8	3.0	2.6	0.9
HMDA/U2	0.60	10.4	2.9	2.9	1.0

structure of ligands, concentration of ions in solution and in the case of $AuCl_4^-$ anions also depends on hydrochloric acid concentration.

Now, we would like to present the influence of ligands length on sorptive properties of anion exchangers towards dicyanoaurate or tetrachloroaurate anions. It is expected that the length of ligands determines their flexibility and hence ability to form chelates with metal ions.

2. Experimental

2.1. Materials

The starting vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymers containing 2 wt% of crosslinker are obtained using suspension polymerization method. The polymerization is carried out in the presence of toluene (50 wt% in respect to the monomers mixture) in order to obtain a material with an expanded gel structure. The VBC/DVB copolymer is swollen in dioxane (1:10 v/v) for 24 h and then aminolyzed with hexamethylenediamine (HMDA) or diethylenetriamine (DETA) (12:1 mol mol^{-1} of Cl in the polymer) by refluxing for 3 h. The characteristics of copolymer modified with HMDA are presented in Table 1 and the one modified with DETA in Table 2. Samples of such polymers containing amino groups in the form of hydrochloride are swollen in small amount of dioxane or DMSO and reacted with the cyanamide (/CA), dimethylcyanamide (/MCA) or carbodiimide (/DCCI) (4 mol mol^{-1} of primary amino groups in the resin) in 15 cm^3 of butanol and 2 cm^3 of concentrated HCl (pH 1–2) per gram of polymer by refluxing for 24 h. The samples /SDC are modified using mixture of reagents (sodium dicyanamide—4:1 mol mol^{-1} of NH_2 groups) in butanol by refluxing for 24 h. After that time beads are placed in a column and washed with butanol, ethanol and diluted HCl. Thus obtained resin is swollen in butanol and subsequently reacted with urotropine /U (2.5 mol excess over the amount of the cyanoguanidine groups in the resin) dissolved in butanol for 24 h at room temperature at pH 1 [25]. The characteristics of resins with these ligands are presented in Tables 1 and 2.

2.2. Methods

Water regain is measured using a centrifugation technique. Nitrogen content is determined by Kiejdahl method. Anion exchange capacity, Z_C, is determined according to the Hecker method [26] and used to calculate ligand concentration.

Affinity of the resins towards $Au(CN)_2^-$ anions is determined by contacting the resins with 50 ppm Au solutions formulated with 0.05N KCN (pH of this solution has been adjusted to 9.6) and towards $AuCl_4^-$ anions by contacting resins samples with 50 ppm solutions at pH 2.6. The molar ratio of the terminal amino groups in ligands to dicyanoaurate or to tetrachloroaurate anions in solution is 10:1 in both cases. After 48 h the polymers are separated by filtration and Au concentration is determined by AAS method

Table 2
Characteristics of anion exchangers with DETA modified ligands (Z_c—anion exchange capacity)

Symbol	Water regain (g g^{-1})	N (mmol g^{-1})	Cl (mmol g^{-1})	Z_c (mmol g^{-1})	Z_L (mmol g^{-1})
DETA	2.49	6.4	5.9	6.0	2.0
DETA/CA1	2.56	6.5	5.6	6.0	2.0
DETA/CA2	2.46	7.6	5.9	6.0	2.0
DETA/CA3	1.74	12.4	5.7	3.4	1.1
DETA/MCA	1.09	9.5	2.6	2.6	0.9
DETA/DCCI	2.32	9.2	5.3	6.1	2.0
DETA/SDC	0.71	2.6	3.2	3.5	1.2
DETA/U	0.70	11.9	4.1	4.4	1.1

with wavelength set at 242.8 nm on a Perkin–Elmer Analyst 100 spectrophotometer. Distribution coefficient, K, is calculated as the ratio of the amount of metal adsorbed by 1 g of dry resin and the amount of metal remaining in 1 cm^3 of solution after sorption.

Sorption of Cu(II) ions is determined by contacting 1×10^{-4} M $Cu(NO_3)_2$ solution in 0.2 M acetate buffer at 3.5 and 5.7 with resin samples. Thus, amount of resin containing 0.05 mmol of ligand is shaken with 10 cm^3 of Cu(II) ions solution for 48 h. Next, polymer is separated by filtration and copper concentration is measured using AAS method with wavelength set at 324.8 nm.

The EPR spectra are recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer operating at X-band and equipped with the Bruker NMR gaussmeter ER 035M and the Hewlett–Packard microwave frequency counter HP 5350B. EPR parameters are calculated by computer simulation of the experimental spectra using Bruker's WIN-EPR SimFonia Software Version 1.25. The EPR experiments are performed at 77 K on the swollen samples of the resins loaded with Cu(II), separated by filtration and air dried. $pH > 5.6$ of Cu(II) solution in equilibrium with the samples was adjusted using NaOH.

3. Results and discussion

3.1. Preparation and characteristics of anion exchangers

In our previous paper we have presented the sorption properties of anion exchangers having guanidyl or biguanidyl groups on ethylenediamine (ETDA) ligands [4–6,8,9]. Sorption of gold as dicyanoaurate or tetrachloroaurate anions on substituted hydrogen atoms in guanidine groups on ethylenodiamine ligands is 2–4 times higher than on anion exchanger synthesized by exchange of chlorine in VBC mers with guanidine or aminoguanidine [8]. Now, we would like to determine the sorption properties of anion exchangers having also the guanidyl groups but attached on the ligands of different length. It can be expected that anion exchangers with longer ligands should be more flexible and have less intramolecular crosslinks.

The anion exchangers with guanidyl and substituted guanidyl groups are prepared by modification of matrix derived from VBC and DVB (2%) copolymer with HMDA or DETA. The amino groups in such obtained ligands were subsequently modified by reaction with:

Cyanamide	NH_2CN	HMDA/CA, DETA/CA
Dimethylcyanamide	$(CH_3)_2NCN$	HMDA/MCA, DETA/MCA
Dicyclohexylcarbodiimide	$H_{11}C_6{-}N{=}C{=}N{-}C_6H_{11}$	HMDA/DCCI, DETA/DCCI
Sodium dicyanamide	NC–N(Na)–CN	HMDA/SDC, DETA/SDC
Sodium dicyanamide and urotropine	NC–N(Na)–CN + $(CH_2)_6N_4$	HMDA/U, DETA/U

The scheme of modification is shown in Fig. 1.

Starting VBC/DVB copolymer contained 5.13 mmol of Cl/g, which is less than 6.83 mmol g^{-1} of the theoretical content calculated based on the composition of the monomer mixture. Reaction of chloromethyl groups with amines is not quantitative and proceeds with 73% yield for HMDA and 60% for DETA. The properties of anion exchangers are presented in Tables 1 and 2. Starting anion exchangers (HMDA and DETA) with $-NH_2$ end groups have high water regain compared to polymer modified with ETDA [8,9]. Ligands concentration (Z_L) determined using Hecker's [26] and Schöniger's [27] methods show that secondary chemical crosslinking is low, lower than in the case of ETDA modification, when non-polar solvents were used [9]. Modification of the anion exchangers is confirmed using FTIR method.

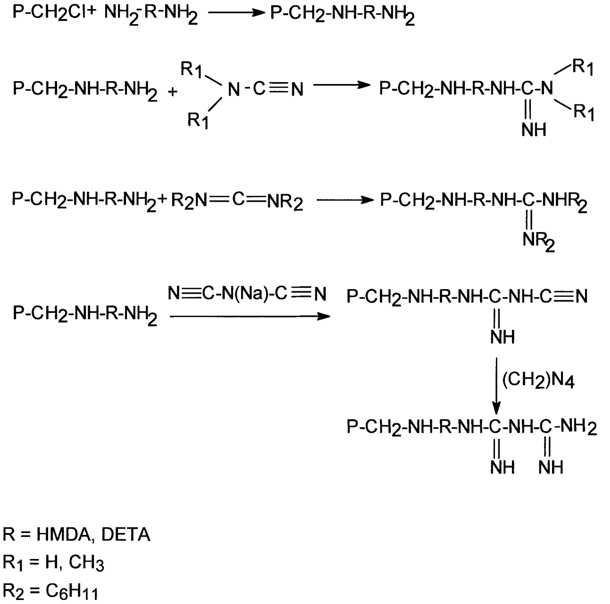

Fig. 1. Scheme of modification.

In the spectrum of parent HMDA resin (with HMDA groups) typical peaks for the polystyrene matrix are observed. These are peaks at 1448, 1490 and 1606 cm^{-1} due to the double conjugated bonds of the phenyl ring, while the strong peak at 1448 cm^{-1} is ascribed to scissoring deformation of CH_2 groups of HMDA. The other strong peak at 1589 cm^{-1}, seen in all the spectra of ion exchangers, is associated with deformation of NH_2^+ ($\delta_{NH_2^+}$) (Fig. 2(I)).

Substitution of terminal $-NH_2$ group with cyanamide gives the anion exchanger with guanidyl groups. The degree of substitution in a mixture of dioxane and butanol, measured by nitrogen analysis, is not too high (for example DETA/CA1 or DETA/CA2). If the reaction is carried out in better solvent like DMSO nitrogen content in samples increases, but the extent of by-reaction increases too. Thus, the concentration of free groups, measured using Hecker's method decreases.

According to Zang and coworkers [28] there are the following characteristic peaks for polymeric guanidine: $\nu_{C=N}$ at 1689–1650 cm^{-1} (stretching vibration), δ_{NH} at

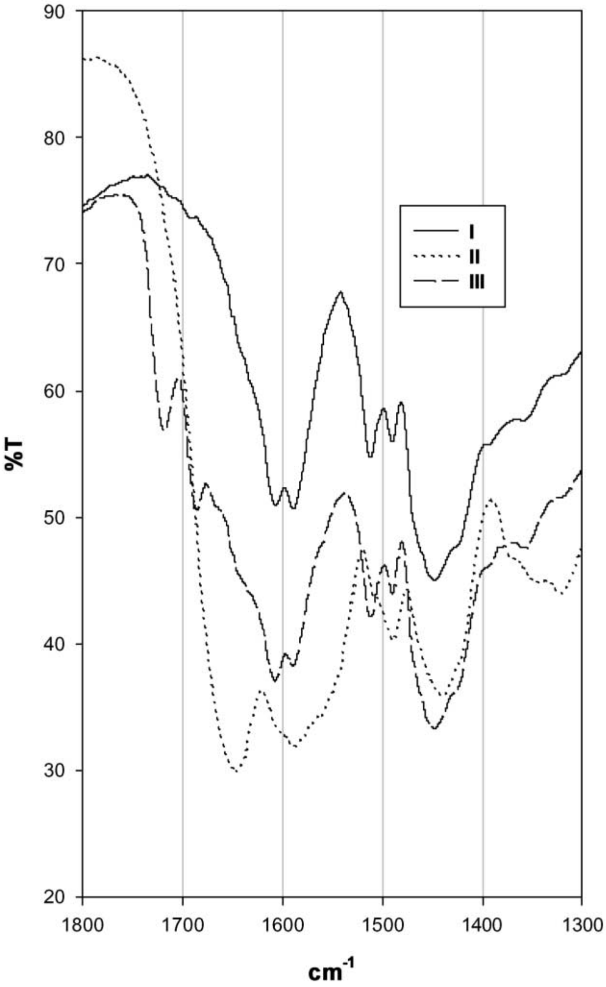

Fig. 2. FTIR spectra of the HMDA anion exchangers: (I) HMDA, (II) HMDA/CA, (III) HMDA/MCA.

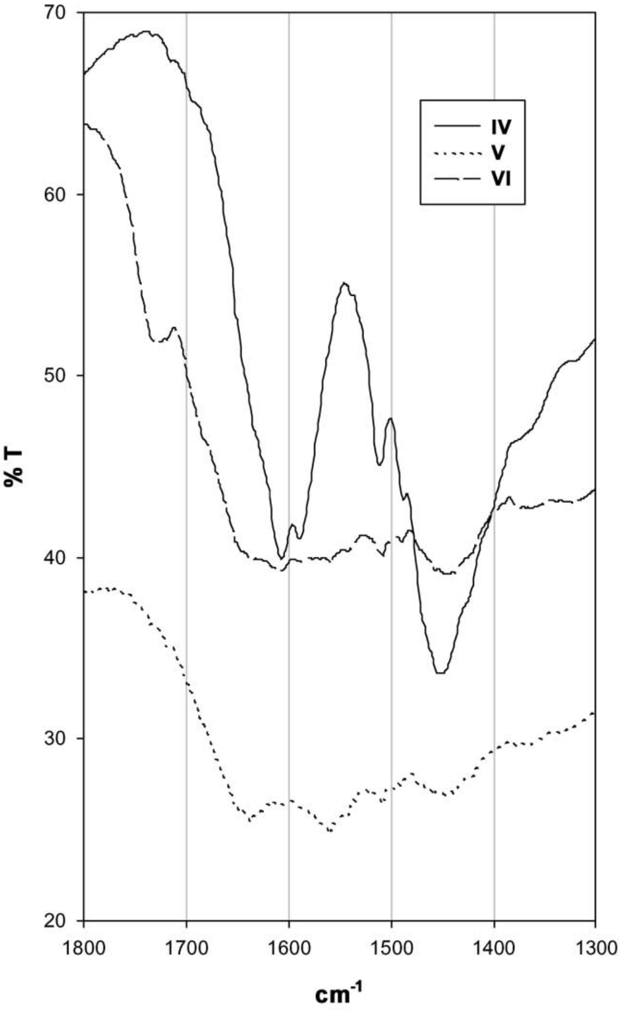

Fig. 3. FTIR spectra of the DETA anion exchangers: (IV) DETA, (V) DETA/SDC, (VI) DETA/U.

about 1640 cm^{-1} (scissoring bending), $\nu_{\mathrm{C-N}}$ at about 1300 cm^{-1} (stretching vibration).

These peaks appear in the spectra of all anion exchangers, but their intensity varies. The intensity of peaks at 1300, 1644 and 1685 cm^{-1} for samples modified with cyanamide (HMDA/CA) is very low, probably due to small degree of transformation (Fig. 2(II)). Cyanamide can appear in tautomeric form as carbodiimide and has ability to react with primary and secondary amino groups what causes intra and inter molecular crosslinks. For the reason of low degree of transformation the swelling of anion exchanger HMDA/CA is similar to that of HMDA.

The higher is substitution of amino groups by MCA (about 1 with reference to amino end groups calculated from nitrogen analysis) the higher intensity of characteristic peaks for HMDA/MCA (Fig. 2(III)). MCA, which has two hydrogen atoms substituted by methyl groups, reacts with primary and secondary amino groups, but cannot create crosslinks between ligands. Water regain of anion exchanger decreases, which is probably due to cycle creation. Carbodiimide DCCI weakly reacts with amino groups, because of steric hindrance created by its bulky, cyclohexyl substituents.

Sodium dicyanamide has the best reactivity towards amino groups. After this transformation a new peak appears at 1558 cm^{-1} as a result of the superposition of two deformation peaks NH_2^+ and doublets for guanidyl and biguanidyl groups (Fig. 3(V)). In addition, a strong and sharp peak appears at 2168 cm^{-1} which can be ascribed to the nitrile groups.

After urotropine attaching, water regain decreases drastictically and remains small. It is probably due to additional crosslinking of a matrix containing amino groups by formaldehyde, which is the product of urotropine decomposition. Two characteristic peaks for biguanidine (1635 and 1560–1510 cm^{-1}) are broadened (Fig. 3(VI)).

3.2. Sorption and EPR of copper(II)

The sorption capacity of DETA and HMDA resins towards dicyanoaurate and tetrachloroaurate anions depends mainly on ability of ligand nitrogen atom donors

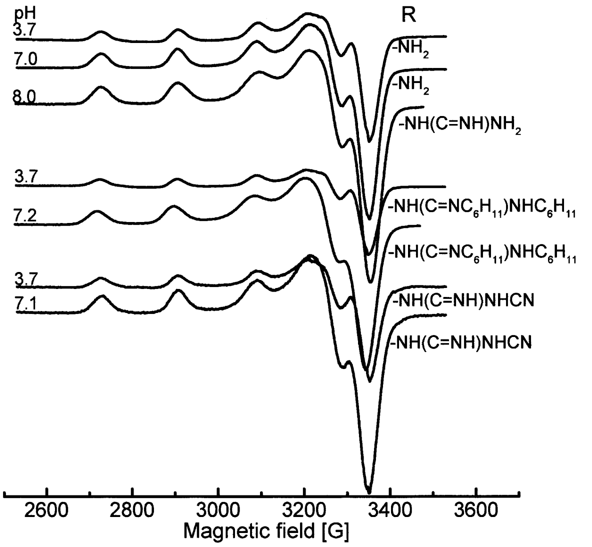

Fig. 4. EPR spectra of DETA anion exchangers with $-NH(CH_2)_2-R$ ligands as a function of pH at 77 K.

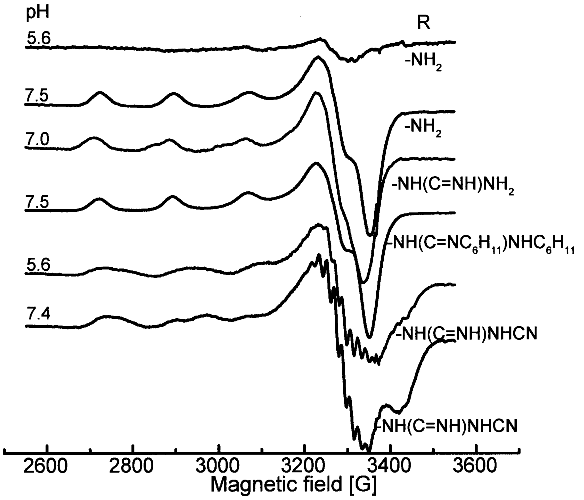

Fig. 5. EPR spectra of HMDA anion exchangers with $-NH(CH_2)_6-R$ ligands as a function of pH at 77 K.

to be protonated and on accessibility of the binding centers for interaction with gold containing anions. These ion-exchanger properties may be indirectly tested using EPR spectroscopy. A competition between Cu(II) ions and protons bound to the nitrogen donors is affected mainly by pH and can be distinctly observed in EPR spectra measured just within the resin matrix. EPR parameters allow to discriminate between Cu(II)-aqua ions and Cu(II) complexes with the resin donor atoms and to determine a mutual relation between complexation ability of DETA and HMDA resins and their sorption properties towards Cu(II) ions.

EPR spectra (Figs. 4 and 5) of axial character are observed for Cu(II) ions bound to DETA and HMDA resins. They indicate that Cu(II) ions immobilized on nitrogen donors form complexes of tetragonal geometry. Hence, values of spectral parameters $g_{||}$ and $A_{||}$, are the main measure of interactions between copper(II) unpaired electron (d_{x2-y2}) and donor atoms in Cu(II) plain.

EPR parameters of Cu(II) complexes with the DETA resins containing guanidyl, biguanidyl or substituted guanidyl groups appeared to be very close to each other independently on pH. Furthermore, the spectra are similar to that observed for a complex formed with non-modified DETA. The values of EPR parameters $g_{||} = 2.228$ and $A_{||} = 185 \times 10^{-4}\ \mathrm{cm}^{-1}$ are between those characteristic for the complex with one EDA ligand ($g_{||} = 2.269$ and $A_{||} = 176 \times 10^{-4}\ \mathrm{cm}^{-1}$, with N_2O_2 donor set) and for the complex with two EDA ($g_{||} = 2.210$ and $A_{||} = 195 \times 10^{-4}\ \mathrm{cm}^{-1}$, with 4N donor set around Cu(II) plane) [8]. Intensity of the spectra of Cu(II) loaded on DETA resins increases manifoldly between pH 3.7 and 7.5 what obviously indicates similar trend in Cu(II) complex concentration. This fully agrees with Cu(II) sorption by DETA resins, which increases significantly upon pH increase (Table 3). Sorption by DETA resins decreases when the ligands content Z_L is lower, suggesting only one coordinating function of the ligands. All the results imply that coordination sphere around Cu(II) is created by one tridentate DETA resins ligand. The number of deprotonated ligands significantly increases as the pH gets higher.

Sorption of Cu(II) ions by HMDA resins is near zero even at pH 5.6. This exceptional feature is presented also by

Table 3
Sorption of Cu(II) from solutions of different pH

Symbol	Water regain (g g^{-1})	Z_L (mmol g^{-1})	Sorption Cu(II) at pH (mg g^{-1})		
			3.7	5.0	5.6
DETA	2.49	2.0	2.6	5.4	9.5
DETA/CA1	2.56	2.0	1.9	3.9	5.6
DETA/CA2	2.46	2.0	0.3	1.4	7.4
DETA/CA3	1.74	1.1	–	–	13.1
DETA/MCA	1.09	0.9	0.6	–	6.1
DETA/DCCI	2.32	2.0	0	–	20.5
DETA/SDC	0.71	1.2	0.8	2.0	3.6
DETA/U	0.70	1.1	0.5	1.6	3.5

Table 4
Sorption of gold on anion exchangers modified with DETA (*K*—amount of gold sorbed by 1 g of polymer divided by amount of gold left in 1 ml solvent at equilibrium)

Symbol	Water regain (g g^{-1})	Z_L (mmol g^{-1})	Sorption $Au(CN)_2^-$ (mg g^{-1})[a]	log *K*	Sorption $AuCl_4^-$ (mg g^{-1})[a]	log *K*
DETA	2.49	2.0	40.3	3.1	87.8	3.9
DETA/CA1	2.56	2.0	35.6	3.0	90.6	3.9
DETA/CA2	2.46	2.0	35.9	3.0	91.6	4.9
DETA/CA3	1.74	1.1	–	–	64.8	4.5
DETA/MCA	1.09	1.0	29.9	3.0	49.2	4.3
DETA/SDC	0.71	1.2	29.4	3.0	66.9	4.3
DETA/U	0.70	1.1	38.7	3.1	79.5	4.9

[a] Calculated as gold, initial concentration of gold—50 ppm.

HMDA/SDC and HMDA/SDC/U resins, which exhibit weak Cu(II) uptake capacity, lower than 1 mg g^{-1} at pH 5.6. EPR spectra of Cu(II) loaded on HMDA resins fully support small potential of HMDA resins in Cu(II) coordination. Spectra of formed complexes are observed only at pH greater than 7. A long distance between nitrogen donors in HMDA precludes their chelate function and as usual in such case, extending number of deprotonated monodentate donors is necessary to form stable complexes. Only HMDA/SDC or HMDA/SDC/U substantially react with Cu(II) at lower pH about 5. For all ligands interacting with Cu(II) ions at pH close to 7 the spectrum with parameters $g_{||} = 2.265$ and $A_{||} = 180 \times 10^{-4}\ \mathrm{cm}^{-1}$ is most likely associated with the complex containing four nitrogen donors of monodentate imine group. Similar EPR parameters are characteristic for Cu(II) complex with four imidazole nitrogens in Cu(II) plane; such coordination was supported additionally by the crystallographic studies [29]. In some cases (for HMDA or HMDA/CA or HMDA/MCA) other weak signal, in equilibrium with that due to the major complex with four nitrogen donors, is observed. Its parameters, $g_{||} = 2.298$ and $A_{||} = 155 \times 10^{-4}\ \mathrm{cm}^{-1}$, suggest that Cu(II) coordination sphere consists of two nitrogen and two oxygens of water molecules.

The EPR spectrum of Cu(II) bound to HMDA/SDC or HMDA/SDC/U ligands already at pH 5.6 consists of signals corresponding to two complexes being in an equilibrium. One of spectra has parameters similar to those stated for all other Cu(II)-HMDA resins. A spectrum of new complex exhibits higher $A_{||}$ and lower $g_{||}$ parameters, $g_{||} = 2.200$ and $A_{||} = 195 \times 10^{-4}\ \mathrm{cm}^{-1}$, implying *NN*′-bidentate nature of the ligands and partly aromatic character of the chelate rings. The spectra at pH 5.6 and 7.8 show, a very rare for Cu(II) immobilized on polymeric ligands, hyperfine splittings due to interaction between copper(II) unpaired electron and four ^{14}N nuclei surrounding Cu(II) in plane. The same spectral properties were observed for EDA modified by unsubsituted guanidine, as a result of Cu(II) chelation through nitrogen of =NH group (beside nitrogen of EDA chain) [8]. A second complex (in equilibrium with a new one) may be formed by terminal amino groups of unmodified HMDA.

3.3. Sorption of dicyanoaurate and tetrachloroaurate

Sorption process under equilibrium depends on the external conditions like pH, concentration of solution and on ratio between ligand end groups and targeted ions. In order to improve understanding of the relations between ligands structure and extent of gold sorption, we were testing all anion exchanger towards dicyanoaurate and tetrachloroaurate anions sorption.

The capacity of DETA-type and HMDA-type ligands towards $AuCl_4^-$ is similar in respect to their Z_L content (Tables 4 and 5). This should be expected taking into account that solution of $AuCl_4^-$ is strongly acidic and the

Table 5
Sorption of gold on the anion exchangers modified with HMDA (*K*—amount of gold sorbed by 1 g of polymer divided by amount of gold left in 1 ml solvent at equilibrium)

Symbol	Water regain (g g^{-1})	Z_L (mmol g^{-1})	Sorption $Au(CN)_2^-$ (mg g^{-1})[a]	log *K*	Sorption $AuCl_4^-$ (mg g^{-1})[a]	log *K*
HMDA	2.43	2.5	42.3	3.2	86.8	4.2
HMDA/CA1	2.46	2.4	36.3	3.1	85.8	4.3
HMDA/CA3	1.72	1.9	–	–	75.6	4.8
HDMA/MCA	1.01	1.1	23.1	3.0	42.6	5.0
HMDA/SDC	0.62	1.4	35.2	3.3	51.9	4.9
HMDA/U1	0.38	0.9	32.7	3.3	51.6	5.4
HMDA/U2	0.60	1.0	43.5	3.6	55.6	5.1

[a] Calculated as gold, initial concentration of gold—50 ppm.

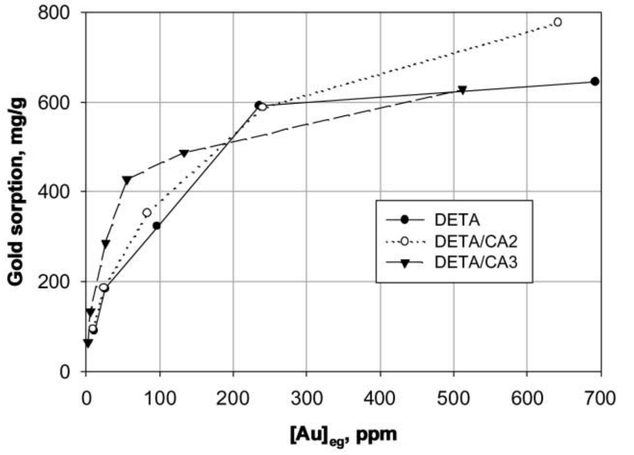

Fig. 6. Sorption isotherms of tetrachloroaurate on DETA anion exchangers.

nitrogens are protonated. The similarity between sorption properties showed by DETA and HMDA resins indicates that only one protonated nitrogen is accessible for interaction with a large $AuCl_4^-$ anions. As the ligand nitrogens are to a high extent protonated, even at pH 5.6, the ability to coordinate Cu(II) ions becomes low for DETA and negligible for HMDA resins. Cu(II) uptake significantly increases with pH increase according to results of EPR studies. On the other hand ligands, in general, show similar efficiency for interacting with $Au(CN)_2^-$ independly on the resin, although the sorption capacities are almost twice smaller that for $AuCl_4^-$. This is in agreement with significant ability of the ligands to coordinate Cu(II) ions, which is proportional to the presence of deprotonated nitrogen donors. The HMDA/SDC and HMDA/U resins, exhibiting greater Cu(II) uptake compared to other HMDA resins, appeared also to be effective sorbents for $AuCl_4^-$ and $Au(CN)_2^-$ what may be treated as evidence of a specific properties of these ligands.

Unexpectedly high is the sorption of dicyanoaurate from 50 ppm solution on anion exchanger with ligands having primary end groups. In such case sorption is even higher than on resins with ETDA ligands [8] and higher than on piperazine resin [3]. The transformation with cyanamide to guanidyl groups, which can be seen from nitrogen content and FITR, proceeds to a small extent and does not influence the sorption properties. The modification of ligand end groups with the sodium dicyanamide occurs with high yield as evidenced by nitrogen content increase (Tables 1 and 2). After treating with urotropine, the anion exchangers with biguanidine groups have been obtained. Low ligands concentration and small water regain is observed, which is due to crosslinking of resins. The sorption of dicyanoaurate on the HMDA/U and DETA/U resins is higher than on other anion exchangers with guanidyl group ligands.

The sorption of tetrachloroaurate anions from acidic solutions (0.1 M HCl) and 50 ppm concentration is proportional to ligand concentrations. Figs. 6 and 7 show correlation between the sorption and $AuCl_4^-$ external solution concentration. All tested resins have good sorptive properties.

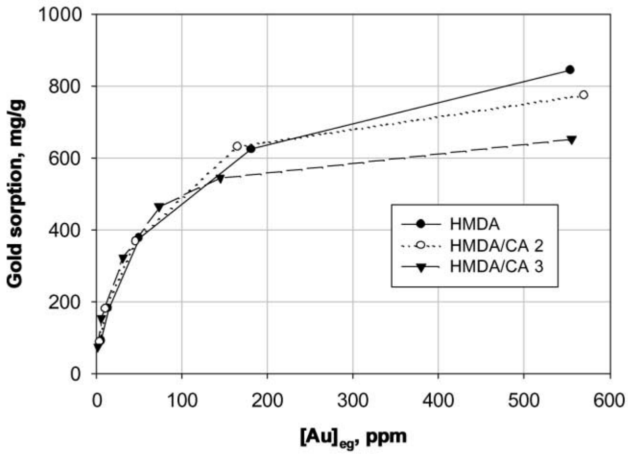

Fig. 7. Sorption isotherms of tetrachloroaurate on HMDA anion exchangers.

4. Conclusions

1. The convenient method of biguanidyl groups introduction into polymer matrix is the reaction of amino groups with dicyanamide.
2. Ligands longer than EDA, such as HDMA and DETA, do not cause significant increase of sorption properties of resins towards dicyanoaurate and tetrachloroaurate anions.
3. The HMDA resins do not sorb Cu(II) cations at pH 5.7, with the exception of HMDA resins modified by sodium dicyanamide, the complex formation is observed in EPR spectra at pH about 7. DETA resins are better sorbents for Cu(II) due to ligands chelating properties; Cu(II) coordination is detected in EPR spectra already at pH 3.6.

Acknowledgements

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